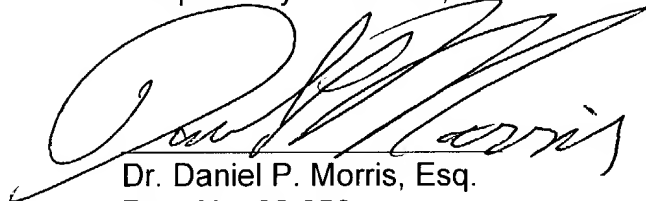


## REMARKS

The attachments are selected papers from the ancestral file history referred to in the Fifth Supplementary Response. Attachment 60 refers to Attachments 1-38 which are the same as Attachments 1-38 of the Fifth Supplementary Response.

Please charge any fee necessary to enter this paper and any previous paper to deposit account 09-0468.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Dr. Daniel P. Morris, Esq.", written over a horizontal line.

Dr. Daniel P. Morris, Esq.  
Reg. No. 32,053  
(914) 945-3217

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598

OCT 10 2000 12:05 PM FROM HRLINGTON 703 412 2033 TO YORKTOWN  
ANSWER, AND 5 BOOKS, REFERENCES IN THE SECOND SUPPLEMENTAL  
APPELLANT'S REPLY TO THE EXAMINER'S ANSWER.

P.03/03

PLEASE STAMP & RETURN TO US  
**RECEIVED**

as an application of: J. G. Bednorz et al. **OCT 10 2000**

For: **TECHNOLOGY CENTER 1700**

Serial No.: 08/303,561 Docket No.: Y0987-0748Y Atty.: DPM

Received in the U.S. Patent & Trademark Office

No. of pages of specification: No. of pages of claims

No. of sheets of drawings:

Declaration is attached to specification.

All fees are charged to our Account No. 09-0469





RECEIVED

NOV 12 1997  
U.S. AIR MAIL  
U.S. AIR MAIL  
U.S. AIR MAIL

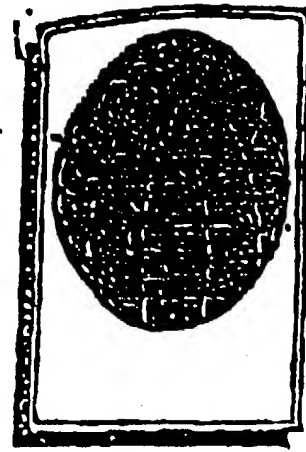
MR. MANNY W. SCHECTER  
IBM CORPORATION  
INTELLECTUAL PROPERTY LAW DEPT.  
P.O. BOX 218  
YORKTOWN HEIGHTS, NEW YORK 10598

IBM Corporation  
1735 S. Jefferson Davis Highway  
Suite 605  
Arlington, Virginia 22202

Fax No.: (703) 412-2099

Tie Line: 8-894-2099

Contact No.: (703) 412-2400 / TL 8-894-2400



Date: 10/10/00

No. Of Pgs Cover: 2

To:

Dan Morris -/0

Jennifer Smith -/0

From: Jay Doyle

X2420

Re:

Y09-87-074BY receipt  
Original to be mailed -

PLEASE MAKE COPIES FOR THOSE PERSONS AT THE SAME FAX NUMBER

<sup>3 copies</sup>  
FILING SECOND SUPPLEMENTAL APPELLANT'S REPLY TO THE EXAMINER'S  
ANSWER, AND 5 BOOKS AS REFERENCES IN THE SECOND SUPPLEMENTAL  
APPELLANT'S REPLY TO THE EXAMINER'S ANSWER.

PLEASE STAMP & RETURN TO US

in re application of: J. G. Bednorz et al.

For: \_\_\_\_\_

Serial No.: 08/303,561; Docket No.: Y0987-074BY Atty.: DPM

Received in the U.S. Patent & Trademark Office

No. of pages of specification:       ; No. of pages of claims       

No. of sheets of drawings:       

Declaration is attached to specification.

All fees are charged to our Account No. 09-0463



**BEFORE THE BOARD OF PATENT APPEALS  
AND INTERFERENCES**

Paper No. 93 <sup>4</sup> DM

**RECEIVED**

**MAR 11 2004**

Application Number: 08/303,561

Filing Date: September 09, 1994

Applicants: Johannes G. Bednorz et al.

Examiner M. Kopec

Daniel P. Morris  
For Appellant

**SECOND SUPPLEMENTAL APPELLANT'S REPLY  
TO THE EXAMINER'S ANSWER**

Appellant's SUBSTITUTE SUPPLEMENTAL APPELLANT'S REPLY TO THE EXAMINER'S ANSWER TEXT ONLY, submitted on August 24, 2000, refers to Attachment C that contains a Table 1 of high T<sub>c</sub> materials from the "CRC Handbook of Chemistry and Physics" 2000-2001 Edition. Table 1 lists 7 references as the source of the information on the 42 high T<sub>c</sub> materials in Table 1. Those references are listed below. Attachments E to K of the Appellant's SUBSTITUTE SUPPLEMENTAL APPELLANT'S REPLY TO THE EXAMINER'S ANSWER TEXT ONLY, submitted on August 24, 2000, contain the title page and table of contents of the books corresponding to references 1-5 respectively. References 6 and 7 are articles, copies of which were in Attachments J and K, respectively, of Appellant's SUBSTITUTE

Application Number: 08/303,561      1      Docket YO987-074BY

**SUPPLEMENTAL APPELLANT'S REPLY TO THE EXAMINER'S ANSWER TEXT**

**ONLY**, submitted on August 24, 2000. Enclosed are the books corresponding to Attachments E (Vols. I and II), F, H and I. The books corresponding to Attachment E (Vol. III) and Attachment G will not be available until late November 2000. They will be submitted to the USPTO when they are received by appellants.

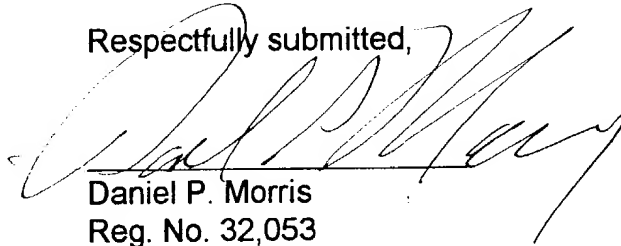
1. Attachment E  
Ginsburg, D.M., Ed., Physical Properties of High-Temperature Superconductors, Vols. I-III, World Scientific, Singapore, 1989-1992.
2. Attachment F  
Rao, C.N.R., Ed., Chemistry of High-Temperature Superconductors, World Scientific, Singapore, 1991.
3. Attachment G  
Shackelford, J.F., The CRC Materials Science and Engineering Handbook, CRC Press, Boca Raton, 1992, 98-99 and 122-123.
4. Attachment H  
Kaldis, E., Ed., Materials and Crystallographic Aspects of HTc-Superconductivity, Kluwer Academic Publ., Dordrecht, The Netherlands, 1992.
5. Attachment I  
Malik, S.K. and Shah, S.S., Ed., Physical and Material Properties of High Temperature Superconductors, Nova Science Publ., Commack, N.Y., 1994.
6. Attachment J  
Chmaissem, O. et al., Physica C230, 231-238, 1994
7. Attachment K  
Antipov E. V. et al., Physica C215, 1-10, 1993, 231-238, 1994

The is no evidence in these references that the 42 high Tc materials of  
Attachment C cannot be made following appellants' teaching.

Appellants request the Board to reverse the examiners rejections of claims  
under 35 USC 112, first paragraph.

Please charge any fee necessary to enter this paper to deposit account  
09-0468.

Respectfully submitted,

A handwritten signature in black ink, appearing to read 'Daniel P. Morris', is written over a horizontal line.

Daniel P. Morris  
Reg. No. 32,053  
(914) 945-3217

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598

**BEFORE THE BOARD OF PATENT APPEALS  
AND INTERFERENCES**

Paper No. \_\_\_\_\_

Application Number: 08/303,561

Filing Date: September 09, 1994

Applicants: Johannes G. Bednorz et al.

Examiner M. Kopec

Daniel P. Morris  
For Appellant

**FOURTH SUPPLEMENTAL APPELLANTS' REPLY  
TO THE EXAMINER'S ANSWER**

**ARGUMENT**

As indicated in Appellant's Request For Postponement of Oral Hearing Scheduled For November 6, 2002, dated November 21, 2002, which was granted by the Order Granting Request To Reset Hearing Date, dated November 6, 2002, attached herewith is a sequential concordance of copies of documentary evidence referred to in Appellants' Brief and Replies which were submitted as attachments and appendixes to papers and affidavits submitted during prosecution. These copies of the concordance is to this Fourth Supplemental Appellants' Reply To The Examiner's Answer. The first pages of the Concordance is marked Concordance and Contains a Table of Contents which lists the documents in the order of first appearance in the Brief and Replies. All page are identified where the document occurs in the Brief and Reply Briefs. Documents in Appendix of The Brief and Reply Briefs are not included in the Concordance.

## ADDITIONAL REMARKS CITING PORTIONS OF THE FILE HISTORY

Claims 24-26, 88-90, 96-102, 109-113, 129-131, 134, 135, 139-142, 145, 149-151, 158, 159, 164-166, 169-170 and 174-177 of the present application have been rejected as not enabled under 35 U.S.C. 112, first paragraph. Appellants disagree for the reasons previously noted. Appellants in addition point out the following.

The present application is a Continuation of 08/060,470 filed on 05/11/93, which is a Continuation of 07/875,003 filed on 04/24/92, which is a Divisional of 07/053,307 filed on 05/22/87 all now abandoned.

In the 07/053,307 ancestral application composition of matter claims were presented for examination. A copy of the Final Rejection referred to below in this application is in Attachment A of this paper.

In the 07/053,307 ancestral application composition of matter, claims 1 through 11 inclusive, 27 through 35 inclusive, 40 through 54 inclusive, 60 through 63 inclusive, and 65 through 68 were finally rejected under 35 U.S.C. 102(b) or in the alternative under 35 U.S.C. 103 as unpatentable over each of a publication by Shaplygin et al. in the Russian Journal of Inorganic chemistry, volume 24, pages 820-824 (1979) ("the Shaplygin et al. publication"); a publication by Nguyen et al. in the Journal of Solid State Chemistry, volume 39, pages 120-127 (1981) ("the Nguyen et al. publication"); a publication by Michel et al. in the Materials Research Bulletin, volume 20, pages 667-671 (1985) ("the 1985 Michel et al. publication"); and a publication by Michel and Raveau in the Revue de Chimie Minerale, volume 21, pages 407-425 (1984) ("the 1984 Michel and Raveau publication"). See the final rejection dated 4-25-1991 in the 07/053,307 ancestral application.

In the 07/053,307 ancestral application, claims 1, 2, 5 through 11 inclusive, 40 through 44 inclusive, 46, 48, 51 through 54 inclusive, 60, 62, and 66 were finally rejected under 35 U.S.C. 102(b) or in the alternative under 35 U.S.C. 103 as unpatentable over a



publication by Perron-Simon et al. in C. R. Acad. Sc. Paris, volume 283, pages 33 through 35 (12 July 1976) ("the Perron-Simon et al. publication"); a publication by Mossner and Kemmler-Scak in the Journal of the Less-Common Metals, volume 105, pages 165 through 168 (1985) ("the Mossner and Kemmler-Sack publication"), a publication by Chincholkar and Vyawahare in Thermal Analysis 6th, volume 2, pages 251 through 256 (1980) ("the Chincholkar and Vyawahare publication"); a publication by Ahmad and Sanyal in Spectroscopy Letters, volume 9, pages 39 through 55 (1976) ("the Ahmad and Sanyal publication"); a publication by Blasse and Corsmit in the Journal of Solid State Chemistry, volume 6, pages 513 through 518 (1973) ("the Blasse and Corsmit publication"); United States Patent No. 3,472,779 to Kurihara et al. ("the Kurihara et al. '779 patent"); a publication by Anderton and Sale in Powder Metallurgy No. 1, pages 14 through 21 (1979) ("the Anderton and Sale publication"). (See the final rejection dated 4-25-1991).

In the 07/053,307 ancestral application the Examiner asserted that the cited references appeared to disclose materials, which inherently provided superconductive properties and assertedly therefore, rendered the claims unpatentable. Appellants rebutted the Examiner's reasons for rejection based on limitations in the claims directed to Appellants' new discovery of the superconductive properties of these materials.

The claims of the present application are directed to methods of flowing a superconducting current in a superconductive composition of matter having a transition temperature greater than 26°K. This is Applicants' discovery for which they received the 1987 Nobel Prize in Physics. The Examiner in the 07/053,307 ancestral application stated by the 35 U.S.C. 102 and 103 rejections therein that persons of skill in the art knew how to make the compositions of matter based on the references cited therein. In that same final rejection the Examiner states at page 4 thereof "these materials appear to be identical to those presently claimed except that the superconductive properties are not disclosed." Applicants discovered the superconductive properties and in the present application are claiming methods using this property. Thus, by the Examiner's reasoning all of the present claims are fully enabled because the Examiner has stated

that the compositions of matter recited in the claims can be made with the knowledge of a person of skill in the art prior to Applicant's filing date. Thus the Examiner, in the 07/053,307 ancestral application, agrees with the Appellants' Arguments and the Affidavits of Shaw, Duncombe, Tsuei, Dinger and Mitzi submitted by Appellant in support of their position that all their claims are enabled. In view thereof, Applicants request the Board to reverse the rejection of the claims under 35 U.S.C. 112, first paragraph as not enabled.

Section 104(b)(3) of 37 CFR states "[i]n rejecting claims the examiner may rely upon admissions by the applicant ... as to any matter affecting patentability". Thus, if Appellant in rebutting the 35 USC 112 rejections made statements adverse to their interests in regards to rebutting the rejections under 35 USC 102 and 103, the Examiner could use these statements to assert that Appellants admitted that their invention was anticipated or obvious. Likewise, if Appellant in rebutting the 35 USC 102 and 103 rejections made statements adverse to their interest in regards to rebutting the rejections under 35 USC 112, the Examiner could use these statements to assert that Appellants admitted that their claims were not enabled or were indefinite. Section 104(b)(3) does not explicitly apply to the Examiner. Not to apply the rational of 37 CFR 104(b)(3) to the Examiner to find that the necessary consequences of the Examiners 35 USC 102 and 103 rejections of the composition of matter claims of the 07/053,307 are that all of the Appellants' claims are enabled would be manifestly unfair and inequitable.

Claims 86, 87, 96-108, 112, 113, 117, 118, 122, 123, 127, 128 and 147 have been rejected as indefinite under 35 U.S.C. 112, second paragraph.

These claims have been rejected under 35 USC 112, second paragraph, as indefinite for using language of the type "rare earth like" and "pervskite-like", etc. As previously stated the Examiner has arbitrarily rejected Appellants' claims without providing a reason for why Appellants' terms are indefinite while similar terms are not indefinite in the claims of many issued patents. Applicants note that article incorporated by reference at page 6 of the specification were published in September 1986 (which lead

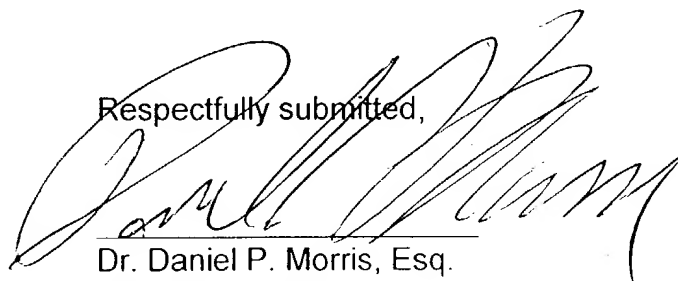
to Appellants' Nobel Prize) and the present application was filed in May 1987 thereby clearly making this terminology part the high Tc superconductor art. As shown this is the vernacular of the field and well understood by persons of skill in the art. Appellants request the Board to reverse the rejections of claims 86, 87, 96-108, 112, 113, 117, 118, 123, 127 and 147 under 35 U.S.C. 112, second paragraph.

Applicants' invention is a pioneering invention. "The Supreme Court in *Westinghouse v. Boyden Power Brake Co.*, 170 U.S. 537, 562 (1898), characterized a pioneering invention as "a distinct step in the progress of the art, distinguished from a mere improvement or perfection of what had gone before." *Texas Instruments ICC* 6 USPQ 2d 1886 (CAFC 1988). Applicants received the 1987 Nobel Prize in Physics for there discovery of superconductivity at Tc greater that or equal to 26°K which is about 8°K higher than the highest Tc previously known. Even though others following Applicants' teaching identified compositions having Tc more than 100°K greater than 26°K only Applicants have received a Nobel Prize for this subject matter. This is because the others followed applicants' teaching to identify these other compositions.

Appellants request the Board to reverse the examiners rejections of claims under 35 USC 112, first paragraph and second paragraph.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

Respectfully submitted,



Dr. Daniel P. Morris, Esq.  
Reg. No. 32,053  
(914) 945-3217

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598

# **ATTACHMENT A**



UNITED STATES DEPARTMENT OF COMMERCE  
Patent and Trademark Office

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

SERIAL NUMBER	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.
07/053,307	05/22/87	BEINORZ	J. 0987-074

EXAMINER
BOYD, J

J. DAVID ELLETT  
181 INTELLECTUAL PROPERTY LAW DEPT.  
P.O. BOX 218  
YORKTOWN HEIGHTS, NY 10598

ART UNIT	PAPER NUMBER
	115

DATE RECEIVED: 04/25/91

DUE 7/25/91

☒ This application has been examined ☒ Responsive to communication filed on 2/13/91 ☒ This action is made final.

A shortened statutory period for response to this action is set to expire 3 month(s) days from the date of this letter.  
Failure to respond within the period for response will cause the application to become abandoned. 35 U.S.C. 133

Part I THE FOLLOWING ATTACHMENT(S) ARE PART OF THIS ACTION:

- |   |   |
|---|---|
| 1. <input type="checkbox"/> Notice of References Cited by Examiner, PTO-892.        | 2. <input type="checkbox"/> Notice re Patent Drawing, PTO-948.                  |
| 3. <input type="checkbox"/> Notice of Art Cited by Applicant, PTO-1449.             | 4. <input type="checkbox"/> Notice of Informal Patent Application, Form PTO-152 |
| 5. <input type="checkbox"/> Information on How to Effect Drawing Changes, PTO-1474. | 6. <input type="checkbox"/>   |

Part II SUMMARY OF ACTION

1. ☒ Claims 1-45 are pending in the application.  
Of the above, claims 12-26, 36-39, 55-59, + 64 are withdrawn from consideration.  
2. ☐ Claims have been canceled.  
3. ☐ Claims are allowed.  
4. ☒ Claims 1-11, 17-35, 40-54, 60-63 + 65-68 are rejected.  
5. ☐ Claims are objected to.  
6. ☐ Claims are subject to restriction or election requirement.  
7. ☐ This application has been filed with informal drawings under 37 C.F.R. 1.85 which are acceptable for examination purposes.  
8. ☐ Formal drawings are required in response to this Office action.  
9. ☐ The corrected or substitute drawings have been received on Under 37 C.F.R. 1.84 these drawings are ☐ acceptable; ☐ not acceptable (see explanation or Notice re Patent Drawing, PTO-948).  
10. ☐ The proposed additional or substitute sheet(s) of drawings, filed on has (have) been ☐ approved by the examiner; ☐ disapproved by the examiner (see explanation).  
11. ☐ The proposed drawing correction, filed has been ☐ approved; ☐ disapproved (see explanation).  
12. ☐ Acknowledgement is made of the claim for priority under U.S.C. 119. The certified copy has ☐ been received ☐ not been received ☐ been filed in parent application, serial no. ; filed on  
13. ☐ Since this application appears to be in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under Ex parte Quayle, 1935 C.D. 11; 453 O.G. 213.  
14. ☐ Other

1. Applicant's election with traverse of Group I in Paper No. 22 is acknowledged. The traversal is on the ground(s) that the claims of Groups I, II and III are not distinct. This is not found persuasive because the Examiner maintains that the superconductive product, process of making and method of use are directed to patently distinct inventions. Although there are broad "process" and "method" claims that appear to encompass a great deal of subject matter, the limitations in the dependent claims distinguish the claims of the Groups I, II and III.

The requirement is still deemed proper and is therefore made FINAL.

2. The objection to the specification and objection of claims 1-11, 27-35, 40-54, 60-63 and 65-68 under 35 USC 112, first paragraph, is maintained.

3. The following is a quotation of the first paragraph of 35 U.S.C. § 112:

The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same and shall set forth the best mode contemplated by the inventor of carrying out his invention.

The specification is objected to under 35 U.S.C. § 112, first paragraph, as failing to provide an enabling disclosure commensurate with the scope of the claims.

4. The Applicants assert that "the scope of the claims as presently worded is reasonable and fully merited" (page 17 of

Art Unit 115

response). The Examiner disagrees. The present claims are broad enough to include a substantial number of inoperable compositions.

5. The rejection of claims 1-11, 27-35, 40-54, 60-63 and 65-68 under 35 USC 112, second paragraph is maintained.

6. Claims 1-11, 27-35, 40-54, 60-63 and 65-68 are rejected under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

7. The amended term "rare earth-like" is vague. With respect to the lack of stoichiometry, Applicants argue the superconductive properties can be measured as the composition is varied. This is unpersuasive because the present claims broad enough to require an undue amount of experimentation.

8. The Examiner maintains that the term "doping" is vague. Neither the claim or the specification discuss the limits of the effective amounts of doping.

9. The Applicants assert that a discussion of "electron-phonon interactions to produce superconductivity" is found in the specification. The Examiner maintains that the term is not adequately explained. The specification fails to teach how one determines how to enhance the "electron-phonon" interactions?

10. The term "at least four elements" is indefinite considering the number of elements in the periodic table.

Serial No. 07/53,307

-4-

Art Unit 115

11. The rejection of claims 1-11, 27-35, 40-54, 60-63 and 65-68 under 35 USC 102/103 is maintained.

12. Claims 1-11, 27-35, 40-54, 60-63 and 65-68 are rejected under 35 U.S.C. § 102(b) as anticipated by or, in the alternative, under 35 U.S.C. § 103 as obvious over each of Shaplygin et.al., Nguyen et.al., Michel et.al. (Mat. Res. Bull. and Revue de Chimie).

13. The Applicants argue that "no prima facie case has been made that the composition anticipates or renders obvious the subject matter" (page 28 of response). The Examiner maintains that these materials appear to be identical to those presently claimed except that the superconductive properties are not disclosed. Applicants have not provided any evidence that the compositions of the cited references are in any way excluded by the language of the present claims, i.e. Applicants have failed to show that these materials are not superconductive. Applicant's composition claims do not appear to exclude these materials.

14. Applicants further argue that under United States patent law they are entitled to claim compositions which might happen to overlap a portion of the concentration ranges broadly recited in the cited references. "The broad statement of a concentration range in the prior art does not necessarily preclude later invention within the concentration range" (page 29 of response). The Examiner fails to understand how Applicant's incredibly broad claims, some of



which require only the presence of a "doped transition metal oxide" (see claim 42), in anyway fall "within" the scope of the compositions disclosed in the prior art. The cited references disclose very specific compositions that not only fall within the scope of the claims, but appear to be identical to those compositions disclosed in the specification as being superconducting. The Examiner maintains that these materials are inherently superconductive and therefore render the claim unpatentable.

15. With respect to Applicants arguments under 35 USC 103 regarding the "question of non-analogous art" and the assertion the cited prior art is irrevelant to the present claim, the Examiner maintains that for the present "composition" claims the references directed to what appear to be identical materials (both in composition and inherent properties) are clearly relevant. The cited individual disclosures appear to be sufficient to maintain the rejection, the Examiner is not relying on any secondary references to modify the teachings in the references.

16. The rejection of claims 1-2, 5-11, 40-44, 46, 48, 51-54, 60, 62 and 66 under 35 USC 102/103 is maintained.

17. Claims 1-2, 5-11, 40-44, 46, 48, 51-54, 60, 62 and 66 are rejected under 35 U.S.C. § 102(b) as anticipated by or, in the alternative, under 35 U.S.C. § 103 as obvious over each of Perron-

Serial No. 07/53,307

-6-

Art Unit 115

Simon et.al., Mossner et.al., Chincholkar et.al., Amad et.al.,  
Blasse et.al., Kurihara et.al. and Anderton et.al.

18. This rejection is maintained for the reasons set forth in the previous paragraphs. The Examiner maintains that the cited references appear to disclose materials which inherently provide superconductive properties and therefore render the present claims unpatentable.

19. **THIS ACTION IS MADE FINAL.** Applicant is reminded of the extension of time policy as set forth in 37 C.F.R. § 1.136(a).

A SHORTENED STATUTORY PERIOD FOR RESPONSE TO THIS FINAL ACTION IS SET TO EXPIRE THREE MONTHS FROM THE DATE OF THIS ACTION. IN THE EVENT A FIRST RESPONSE IS FILED WITHIN TWO MONTHS OF THE MAILING DATE OF THIS FINAL ACTION AND THE ADVISORY ACTION IS NOT MAILED UNTIL AFTER THE END OF THE THREE-MONTH SHORTENED STATUTORY PERIOD, THEN THE SHORTENED STATUTORY PERIOD WILL EXPIRE ON THE DATE THE ADVISORY ACTION IS MAILED, AND ANY EXTENSION FEE PURSUANT TO 37 C.F.R. § 1.136(a) WILL BE CALCULATED FROM THE MAILING DATE OF THE ADVISORY ACTION. IN NO EVENT WILL THE STATUTORY PERIOD FOR RESPONSE EXPIRE LATER THAN SIX MONTHS FROM THE DATE OF THIS FINAL ACTION.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to John Boyd whose telephone number is (703) 308-3314.

Any inquiry of a general nature or relating to the status of this application should be directed to the Group receptionist whose telephone number is (703) 308-0661.

Serial No. 07/53,307

-7-

Art Unit 115

  
J. Boyd

April 24, 1991

PAUL LIEBERMAN  
SUPERVISORY PRIMARY EXAMINER  
ART UNIT 115

**CONCORDANCE  
TABLE OF CONTENTS**

- 1 European Patent Application 0 275 343 A1.  
Pages 7, 11, 12, 13, 14, 16 and 18.
- 2 Applicants' paper submitted April 11, 1996.  
Pages 7 and 26.
- 3 Z. Phys. B. - Condensed Matter 64, pages 189-193, (1986).  
Pages 10, 11, 16, 17, 23, 24, 30, 31, 33, 36, 37, 49, 50, 74, 75, 94 and 109.  
Reply Page 64.
- 4 Applicants' Response filed March 6, 1997 (Paper #59).  
Page 17.
- 5 Attachment C of Applicants' Response dated September 25, 1995. (Book by  
M. von Laue).  
Page 20.  
Reply Page 21.
- 6 Asahi Shinbaum Article.  
Pages 21, 22, 25, 26, 28, 30, 31, 33, 34, 35, 36, 37, 38, 39, 41, 47, 48, 49, 50,  
51, 52, 74, 91 and 114.
- 7 Attachment K of Applicants' Response dated December 27, 1998.  
Pages 23 and 24.
- 8 Applicants' Response dated December 18, 1998.  
Page 24.
- 9 Applicants' Argument filed January 3, 1996 (Paper #50).  
Page 26.
- 10 Affidavit of Chang C. Tsuei dated January 2, 1996 and filed January 3, 1996  
(Paper #52).  
Page 26.
- 10A Declaration of co-inventors, J. G. Bednorz and K. A. Mueller dated  
March 21, 1988, mailed to USPTO on June 22, 1988.  
Page 41.
- 11 Declaration of Alexis P. Malozemoff signed March 30, 1988.  
Page 41.
- 12 Declaration of Cheng-Chung John Chi dated March 29, 1988 and  
signed March 30, 1988.  
Page 42.

**CONCORDANCE**  
**TABLE OF CONTENTS**

- 13 Declaration of Sung IL Park dated March 29, 1988 and signed March 30, 1988.  
Page 42.
- 14 Declaration of Chang C. Tsuei dated March 29, 1988 and signed  
March 30, 1988.  
Page 43.
- 15 Declaration of Dr. Richard L. Green dated March 29, 1988 and signed  
March 30, 1988.  
Pages 43 and 44.
- 15A Article of B. Raveau, Mat. Res. Bull., Vol. 20, pages 667-671, 1985.  
Page 58.
- 15B Article of C. Michel et al., Revue De Chimie Minerale, Vol. 21, No. 4,  
pages 407-425, (1984).  
Page 58.
- 16 Affidavit of David B. Mitzi dated and signed on December 15, 1998.  
Pages 60, 61, 64, 66, 68, 71, 74, 93, 94, 96, 98 and 100.  
Reply Pages 25, 38, 51 and 58.
- 17 Affidavit of Timothy Dinger dated December 15, 1998 and signed  
December 16, 1998.  
Pages 60, 61, 64, 66, 68, 71, 74, 93, 94, 96, 98 and 100.  
Reply Pages 25, 38, 51, 58 and 59.
- 18 Affidavit of Chang C. Tsuei dated December 15, 1998 and signed  
December 16, 1998.  
Pages 60, 61, 64, 66, 68, 71, 74, 84, 93, 94, 96, 98 and 100.  
Reply Pages 25, 38, 51, 58 and 59.
- 19 Affidavit of Thomas M. Shaw dated December 15, 1998 and signed  
December 14, 1998.  
Pages 60, 61, 64, 66, 68, 71, 74, 84, 85, 93, 94, 95, 96, 98 and 100.  
Reply Pages 25, 38, 51, 58 and 59.
- 20 Affidavit of Peter R. Duncombe dated and signed on December 18, 1998.  
Pages 60, 61, 64, 66, 68, 71, 74, 84, 85, 89, 93, 94, 95, 96, 98 and 100.  
Reply Pages 25, 38, 51, 58, 59 and 66.
- 21 Book of Charles P. Poole, Jr.  
Pages 60, 61, 64, 66, 71, 74, 95, 96, 98, 99, 100 and 107.  
Reply Pages 3, 21, 25, 38, 39, 46, 51, 54, 55, 56, 57, 58, 59, 65 and 66.

CONCORDANCE  
TABLE OF CONTENTS

- 22     Affidavit of James W. Leonard Under 37 CRF 1.132 submitted December 15, 1998.  
       Page 75.  
       Reply Page 61.
  
- 23     Attachment A of Applicants' Response dated May 14, 1998.  
       Pages 96 and 97.
  
- 24     Attachment H of Applicants' Response dated November 28, 1997.  
       Pages 96 and 97.
  
- 25     Attachment A of Applicants' Response dated November 28, 1997.  
       Page 105.
  
- 26     Attachment B of Applicants' Response dated November 28, 1997.  
       Page 105.
  
- 27     Attachment C of Applicants' Response dated November 28, 1997.  
       Page 106.
  
- 28     Attachment D of Applicants' Response dated November 28, 1997.  
       Page 106.
  
- 29     Attachment E of Applicants' Response dated November 28, 1997.  
       Page 106.
  
- 30     Attachment F of Applicants' Response dated November 28, 1997.  
       Page 106.
  
- 31     Attachment I of Applicants' Response dated November 28, 1997.  
       Page 107.
  
- 32     Attachment A of Applicants' Response dated December 27, 1997.  
       Page 107.
  
- 33     Attachments B through J of Applicants' Response dated December 27, 1997.  
       Pages 107 and 108.
  
- 34     Attachment M of Applicants' Response dated November 28, 1997.  
       Page 109.
  
- 35     Attachment A of Applicants' Response dated December 22, 1998.  
       Page 110.

CONCORDANCE  
TABLE OF CONTENTS

- 36 Attachment B of Applicants' Response dated December 22, 1998.  
Page 110.
- 37 Attachment C of Applicants' Response dated December 22, 1998.  
Page 110.
- 38 Attachment D of Applicants' Response dated December 22, 1998.  
Page 110.

Filing Third Supplemental Appellant's Reply To The  
Examiner's Answer (3 Copies), reference book entitled  
"CRC Materials Science And Engineering Handbook"  
3rd Edition, by Shackelford et al., and reference  
entitled "Physical Properties Of High Temperature  
Superconductors III" by Donald M. Ginsberg.

Re application of: Johannes G. Bednorz et al.

For: NEW SUPERCONDUCTIVE COMPOUNDS  
HAVING HIGH TRANSITION TEMPERATURE, AND  
METHODS FOR THEIR USE AND PREPARATION

Serial No.: 08/303,561

Docket No.: YO987-074BY Attorney: DPM

All fees are charged to our Account No. 09-0468

Filing Third Supplemental Appellant's Reply To The  
Examiner's Answer (3 Copies), reference book entitled  
"CRC Materials Science And Engineering Handbook"  
3rd Edition, by Shackelford et al., and reference  
entitled "Physical Properties Of High Temperature  
Superconductors III" by Donald M. Ginsberg.

Re application of: Johannes G. Bednorz et al.

For: NEW SUPERCONDUCTIVE COMPOUNDS  
HAVING HIGH TRANSITION TEMPERATURE, AND  
METHODS FOR THEIR USE AND PREPARATION

Serial No.: 08/303,561

Docket No.: YO987-074BY Attorney: DPM

All fees are charged to our Account No. 09-0468

TECHNICAL CENTER 1700  
FEB 23 4 00 PM '98



**BEFORE THE BOARD OF PATENT APPEALS  
AND INTERFERENCES**

Paper No. 94

Application Number: 08/303,561

Filing Date: September 09, 1994

Applicants: Johannes G. Bednorz et al.

Examiner M. Kopec

Daniel P. Morris  
For Appellant

**THIRD SUPPLEMENTAL APPELLANT'S REPLY  
TO THE EXAMINER'S ANSWER**

Appellant's SUBSTITUTE SUPPLEMENTAL APPELLANT'S REPLY TO THE EXAMINER'S ANSWER TEXT ONLY, submitted on August 24, 2000, refers to Attachment C that contains a Table 1 of high T<sub>c</sub> materials from the "CRC Handbook of Chemistry and Physics" 2000-2001 Edition. Table 1 lists 7 references as the source of the information on the 42 high T<sub>c</sub> materials in Table 1. Those references are listed below. The books corresponding to Attachments E (Vols. I and II), F, H and I were submitted with Appellants' SECOND SUPPLEMENTAL REPLY TO EXAMINER'S ANSWER submitted on October 6, 2000, received by Technology Center 1700 on October 10, 2000. The books corresponding to Attachment E (Vol. III) and Attachment G are submitted herewith. A photocopy of Attachment E (Vol. III) is submitted herewith since although Appellants' have ordered this book from the publisher some time ago, it is not clear that the publisher intends on reprinting this book, which if received will be submitted to the USPTO.

1. Attachment E  
Ginsberg, D.M., Ed., Physical Properties of High-Temperature Superconductors, Vols. I-III, World Scientific, Singapore, 1989-1992.
2. Attachment F  
Rao, C.N.R., Ed., Chemistry of High-Temperature Superconductors, World Scientific, Singapore, 1991.
3. Attachment G  
Shackelford, J. F. and Alexander, W., CRC Materials Science and Engineering Handbook, CRC Press, Boca Raton, 1992, 98-99 and 122-123.
4. Attachment H  
Kaldis, E., Ed., Materials and Crystallographic Aspects of HTc-Superconductivity, Kluwer Academic Publ., Dordrecht, The Netherlands, 1992.
5. Attachment I  
Malik, S.K. and Shah, S.S., Ed., Physical and Material Properties of High Temperature Superconductors, Nova Science Publ., Commack, N.Y., 1994.
6. Attachment J  
Chmaissem, O. et al., Physica C230, 231-238, 1994
7. Attachment K  
Antipov E. V. et al., Physica C215, 1-10, 1993, 231-238, 1994

The is no evidence in these references that the 42 high T<sub>c</sub> materials of Attachment C cannot be made following appellants' teaching.

#### **SUMMARY OF THE QUESTIONS RAISED BY THIS APPEAL**

A number of Appellants' claims have been rejected under 35 USC 112, first paragraph, as not enabled by Appellants' specification. The Examiner has given these reasons in support of this rejection: 1) the Examiner's unsupported statements that the art of high T<sub>c</sub> superconductivity is unpredictable; 2) the Examiner's unsupported statement that the theory of high T<sub>c</sub> superconductivity is not well understood; and 3) the

Examiner points to examples cited in Appellants' specification which do not show superconductivity greater than 26°K. The Examiner has provided no support for reasons 1 and 2 in response to Appellant's request that the Examiner provide evidence in support thereof or an Examiner's Affidavit in support thereof as required by 37 CFR 104(d)(2). The Examiner provided neither. Thus, reasons 1 and 2 are the Examiner's unsupported opinion and therefore reasons 1 and 2 should be disregarded by the Board. Appellant's examples that do not have a  $T_c > 26^\circ\text{K}$  (Reason 3) do not support the Examiner's lack of enablement rejection in view of the decisions cited by Appellants, in particular, *In re Angstadt*, *Amgen v. Chugai Pharmaceutical Co.* and *In re Wands*. Appellants have provided extensive evidence in support of their view that their claims are enabled: 1) the five affidavits of Tzui, Dinger, Duncombe, Shaw and Mitzi, 2) the books and articles cited in these affidavits, 3) the book of Poole that states that the reason so much work was done in such a short period of time after Appellants' first discovery was that the high  $T_c$  materials were easy to make using well known fabrication techniques, 4) the article of Rao et al. entitled "Synthesis of Cuprate Superconductors" which cite numerous species of high  $T_c$  materials which can be made according to Appellants' teaching and 5) the CRC Handbook of Chemistry and Physics which cites numerous species of high  $T_c$  materials which can be made according to Appellants' teaching. Many of the species in 4 and 5 are not specifically recited in Appellants' specification, but they come within the genus of Appellants' claims that have been rejected as not enabled. Moreover, there is no evidence of record that a person of skill in the art cannot, without undue experimentation, make these species following Appellants' teaching. The Examiner has not denied that Appellants' extensive proof shows that a person of skill in the art can fabricate these species following Appellants' teaching. Under *In re Angstadt* and *In re Wands* it is Examiner's burden to establish that undue experimentation is needed to practice Appellants' claimed invention. The Examiner has made no attempt to satisfy this burden.

As stated all of Appellants' claims except for one was rejected in the final rejection as anticipated or obvious over the *Asahi Shinbum* article under 35 USC 102 and 103. In the Examiner's Answer, these rejections were found moot in view of the

new Examiner agreeing that Appellants effectively swore behind the date of this article as alleged by Appellants earlier in the prosecution of this application. The Examiner has not withdrawn the 35 USC 102 and 103 rejections. Thus as alleged by Appellants from very early in the prosecution of this application, by these rejections, the Examiner has necessarily and unambiguously found all of Appellants' claims enabled. As stated, the Asahi Shinbum article derives its enablement from Appellants' publication which was published less than a year before Appellants' filing date and which is incorporated by reference in Appellants' specification. For a reference to anticipate a claimed invention the reference must enable from the teaching therein a person of skill in the art to practice the alleged anticipated claims and for a single reference to render obvious a claimed invention the single reference must enable a person of skill in the art to practice the alleged obvious claims from the teaching of that reference in combination with what is know to a person of skill in the art. Thus, all of Appellants' claims that were rejected under 35 USC 102 and 103 over the Asahi Shinbum article must be fully enabled by the Examiner's own rational.

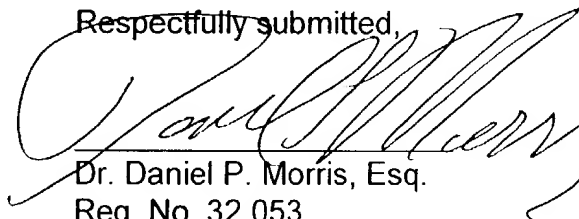
Section 104(b)(3) of 37 CFR states "[i]n rejecting claims the examiner may rely upon admissions by the applicant ... as to any matter affecting patentability". Thus, if Appellant in rebutting the 35 USC 112 rejections made statements adverse to their interests in regards to rebutting the rejections under 35 USC 102 and 103, the Examiner could use these statements to assert that Appellants admitted that their invention was anticipated or obvious. Likewise, if Appellant in rebutting the 35 USC 102 and 103 rejections made statements adverse to their interest in regards to rebutting the rejections under 35 USC 112, the Examiner could use these statements to assert that Appellants admitted that their claims were not enabled or were indefinite. Section 104(b)(3) does not explicitly apply to the Examiner. Not to apply the rational of 37 CFR 104(b)(3) to the Examiner to find that the necessary consequences of the Examiners 35 USC 102 and 103 rejections are that all of the Appellants' claims are enabled would be manifestly unfair and inequitable.

Appellants' claims have been rejected under 35 USC 112, second paragraph, as indefinite for using language of the type "rare earth like" and "pervskite-like", etc. As shown by Appellants, the claims of many issued US Patents use such terms. The Examiner has arbitrarily rejected Appellants' claims without providing a reason for why Appellants' terms are indefinite while similar terms are not indefinite in the claims of these many issued patents.

Appellants request the Board to reverse the examiners rejections of claims under 35 USC 112, first paragraph and second paragraph.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

Respectfully submitted,



Dr. Daniel P. Morris, Esq.  
Reg. No. 32,053  
(914) 945-3217

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598

**BEFORE THE BOARD OF PATENT APPEALS  
AND INTERFERENCES**

Paper No. 93

Application Number: 08/303,561

Filing Date: September 09, 1994

Applicants: Johannes G. Bednorz et al.                      Examiner M. Kopec

Daniel P. Morris  
For Appellant

**SUBSTITUTE SUPPLEMENTAL  
APPELLANT'S REPLY TO THE EXAMINER'S ANSWER  
TEXT ONLY**

In the appellants' reply reference was made to the article "Synthesis of Cuprate Superconductors" by Rao et al., IOP Publishing Ltd. 1993. A copy of this article is in Attachment C to the reply brief. This article lists in Table 1 the properties of 29 cuprate superconductors made according to appellants teaching. Twelve (#'s 1, 8-13, 16, 17, 20, 21, 27 and 28) of those listed do not come within the scope of the claims allowed by the examiner. Only three of the 29 have a  $T_c < 26^\circ\text{K}$ . Those twelve do not contain one or more of a rare earth, a group IIIB element or an alkaline earth element. It is thus clear that broader claims than allowed in the answer should be allowed since it is clear that the allowed claims can be avoided following appellants' teaching without undue experimentation.

The article of Rao et al. in the first sentence of the introduction citing appellants' article - which is incorporated by reference in their application - acknowledges that appellants' initiated the field of high Tc superconductivity. Appellants further note that the Rao article acknowledges that "a large variety of oxides" are prepared by the general principles of ceramic science and that appellants discovered that metal oxides are high Tc superconductors.

Citing reference 5 therein - the book "New Directions in Solid State Chemistry", Rao et al. 1989 (Cambridge; Cambridge University Press) for which there is a 1986 edition which predates appellants filing date Rao (See Attachment B) - Rao et al. states:

Several methods of synthesis have been employed for preparing cuprates, with the objective of obtaining pure monophasic products with good superconducting characteristics [3, 4]. The most common method of synthesis of cuprate superconductors is the traditional ceramic method which has been employed for the preparation of a large variety of oxide materials [5]. Although the ceramic method has yielded many of the cuprates with satisfactory characteristics, different synthetic strategies have become necessary in order to control factors such as the cation composition, oxygen stoichiometry, cation oxidation states and carrier concentration. Specifically noteworthy amongst these methods are

chemical or solution routes which permit better mixing of the constituent cations in order to reduce the diffusion distance in the solid state [5, 6]. Such methods include coprecipitation, use of precursors, the sol-gel method and the use of alkali fluxes. The combustion method or self-propagating high-temperature synthesis (SHS) has also been employed.

Reference 5 is another example of a reference to the general principles of ceramic science incorporated into appellants' teaching. The Rao et al. article states that the 29 materials reported on in the article and listed in Table 1 are fabricated using the general principles of ceramic science. Moreover, the Rao article states that these materials are fabricated by what the Rao article calls the "ceramic method" which is the preferred embodiment in appellants' specification, yet 12 of the 29 materials in Table 1 do not come within the scope of the claims allowed by the examiner in the answer. Thus known examples fabricated according to appellants' teaching will not be literally infringed by the Rao, Duncombe and Poole examples.

In Attachment A there are copies of the table of contents and Chapter 3 the 1989 edition of reference 5. Chapter 3 is entitled "Preparative Strategies". In Attachment B there are copies of the table of contents and Chapter 3 of the 1986 edition of reference 5. Chapter 3 in each edition is substantially the same. Since the publication date of the 1986 edition is before appellants filing date, all 29 of the high T<sub>c</sub> materials in Table



1. of the Rao article are made according to the general principals of ceramic science as taught by appellants.

Attachment C is a Table of high Tc materials from the "CRC Handbook of Chemistry and Physics" 2000-2001 Edition. Attachment D is a copy of this table with hand written numbers to the left of the materials. There are a total of 42 materials listed in Table 1 (those marked with an asterisk in the table in Attachment D #s 1, 7-13, 16-18, 20, 21, 27, 28, 30, 31 and 41-44) of which 21 do not contain one or more of a rare earth, a group III element or an alkaline earth element. Yet all 42 are made according to the general principals of ceramic science taught by appellants. Two of the 42 materials have a Tc of 25K. Thus a person of skill in the art following appellants' teaching can fabricate materials which do not infringe the claims allowed by the examiner but do not infringe claims not allowed by the examiner.

Table 1 in attachment C list 7 references as the source of the information on the 42 high Tc materials. Those references are listed below. For references 1-5 Attachments E to K, respectively, contain the title page and table of contents of the corresponding book. References 6 and 7 are articles, copies of which are in Attachments J and K respectively.

1. Attachment E  
Ginsburg, D.M., Ed., Physical Properties of High-Temperature Superconductors, Vols. I-III, World Scientific, Singapore, 1989-1992.

2. Attachment F  
Rao, C.N.R., Ed., Chemistry of High-Temperature Superconductors, World Scientific, Singapore, 1991.

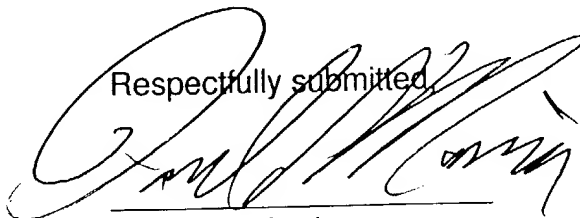
3. Attachment G  
Shackelford, J.F., The CRC Materials Science and Engineering Handbook, CRC Press, Boca Raton, 1992, 98-99 and 122-123.
4. Attachment H  
Kaldis, E., Ed., Materials and Crystallographic Aspects of HTc-Superconductivity, Kluwer Academic Publ., Dordrecht, The Netherlands, 1992.
5. Attachment I  
Malik, S.K. and Shah, S.S., Ed., Physical and Material Properties of High Temperature Superconductors, Nova Science Publ., Commack, N.Y., 1994.
6. Attachment J  
Chmaissem, O. et al., Physica C230, 231-238, 1994
7. Attachment K  
Antipov E. V. et al., Physica C215, 1-10, 1993, 231-238, 1994

The is no evidence in these references that the 42 high Tc materials of Attachment C cannot be made following appellants' teaching.

Appellants request the Board to reverse the examiners rejections of claims under 35 USC 112, first paragraph.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

Respectfully submitted,



Daniel P. Morris  
Reg. No. 32,053  
(914) 945-3217

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598



UNITED STATES DEPARTMENT OF COMMERCE  
Patent and Trademark Office

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.
08/303,561	09/09/94	BEDNORZ	Y0987074BY (US4)

IM22/1024  
DANIEL P MORRIS  
IBM CORPORATION  
INTELLECTUAL PROPERTY LAW DEPARTMENT  
P O BOX 218  
YORKTOWN HEIGHTS NY 10598

EXAMINER	
KOPEC-M	
ART UNIT	PAPER NUMBER
1751	93

DATE MAILED:

10/24/00

Please find below a communication from the EXAMINER in charge of the application.

Commissioner of Patents.


The reply brief filed 7/19/00, Supplemental Reply Brief filed 8/7/00 and Second Supplemental Reply Brief filed 10/10/00 have been entered and considered. The application has been forwarded to the Board of Patent Appeals and Interferences for decision on the appeal.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Mark Kopec whose telephone number is (703) 308-1088. The examiner can normally be reached on Monday-Thursday from 7:30 AM - 6:00 PM.

If reasonable attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Dr. Yogendra Gupta, can be reached on (703) 308-4708.

The official fax phone numbers for this Group are (703) 305-7718 and 305-3599 (for after-final submissions).

Any inquiry of a general nature or relating to the status of this application should be directed to the Group receptionist whose telephone number is (703) 308-0661.

  
Mark Kopec  
Primary Examiner

Mark Kopec  
October 23, 2000



UNITED STATES DEPARTMENT OF COMMERCE  
Patent and Trademark Office

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.
087303,551	07/19/94	BEDNORZ J	Y0987074BY

IM51/1127  
DANIEL P. NORRIS  
IBM CORPORATION  
INTELLECTUAL PROPERTY LAW DEPARTMENT  
P.O. BOX 218  
YONKONN HEIGHTS NY 10598

EXAMINER	
KOPEC, M	
ART UNIT	PAPER NUMBER
1751	

DATE MAILED: 11/27/00

Please find below a communication from the EXAMINER in charge of the application.

Commissioner of Patents.

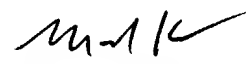
The SUBSTITUTE SUPPLEMENTA reply brief filed 8/28/00 have been entered and considered. The application has been forwarded to the Board of Patent Appeals and Interferences for decision on the appeal.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Mark Kopec whose telephone number is (703) 308-1088. The examiner can normally be reached on Monday-Thursday from 7:30 AM - 6:00 PM.

If reasonable attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Dr. Yogendra Gupta, can be reached on (703) 308-4708.

The official fax phone numbers for this Group are (703) 305-7718 and 305-3599 (for after-final submissions).

Any inquiry of a general nature or relating to the status of this application should be directed to the Group receptionist whose telephone number is (703) 308-0661.

  
Mark Kopec  
Primary Examiner

Mark Kopec  
November 27, 2000

FILING LETTER WITH ATTACHMENT A (3 COPIES), SUBSTITUTE  
SUPPLEMENTAL APPELLANT'S REPLY TO EXAMINER'S ANSWER TEXT ONLY  
(3 COPIES), AND CERTIFICATE OF MAILING.

DATE OF DEPOSIT: AUGUST 24, 2000

PLEASE STAMP & RETURN TO US

(In re application of: BEDNORZ ET AL.

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION ...

Serial No.: 08/303,561; Docket No.: Y0987-074BY Atty.: DPM

Received in the U.S. Patent & Trademark Office: \_\_\_\_\_

No. of pages of specification \_\_\_\_: No. of pages of claims \_\_\_\_

No. of sheets of drawings: \_\_\_\_\_

Declaration is attached to specification.

All fees are charged to our Account No. 09-0468

FILING LETTER WITH ATTACHMENT A (3 COPIES), SUBSTITUTE  
SUPPLEMENTAL APPELLANT'S REPLY TO EXAMINER'S ANSWER TEXT ONLY  
(3 COPIES), AND CERTIFICATE OF MAILING.

DATE OF DEPOSIT: AUGUST 24, 2000

PLEASE STAMP & RETURN TO US

(In re application of: BEDNORZ ET AL.

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION ...

Serial No.: 08/303,561; Docket No.: Y0987-074BY Atty.: DPM

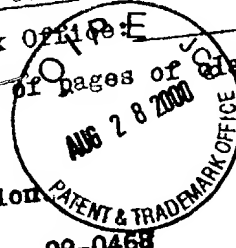
Received in the U.S. Patent & Trademark Office: \_\_\_\_\_

No. of pages of specification \_\_\_\_: No. of pages of claims \_\_\_\_

No. of sheets of drawings: \_\_\_\_\_

Declaration is attached to specification.

All fees are charged to our Account No. 09-0468



**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Date: August 24, 2000

Applicants: Bednorz et al.

Docket: YO987-074BY

Serial No.: 08/303,561

Group Art Unit: 1751

Filed: 09/09/94

Examiner: M. Kopec

For: New Superconductive Compounds Having High Transition  
Temperature, and Methods For Their Use and Preparation

Assistant Commissioner for Patents  
Washington, D. C. 20231

**CERTIFICATE OF MAILING UNDER 37 CFR 1.8 (a)**

I hereby certify that the attached correspondence comprising:

Letter with Attachment A (3 copies)

Substitute Supplemental Appellant's Reply to Examiner's Answer Text Only (3 copies)

Return Postcard

is being deposited with the United States Postal Service as first class mail in an envelope addressed to:

**Assistant Commissioner for Patents  
Washington, D.C. 20231**

on August 24, 2000

Jennifer A. Smith

(Type or printed name of person mailing paper or fee)

  
(Signature of person mailing paper or fee)

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Date: August 24, 2000

Applicants: Bednorz et al.

Docket: YO987-074BY

Serial No.: 08/303,561

Group Art Unit: 1751

Filed: 09/09/94

Examiner: M. Kopec

For: New Superconductive Compounds Having High Transition  
Temperature, and Methods For Their Use and Preparation

Assistant Commissioner for Patents  
Washington, D. C. 20231

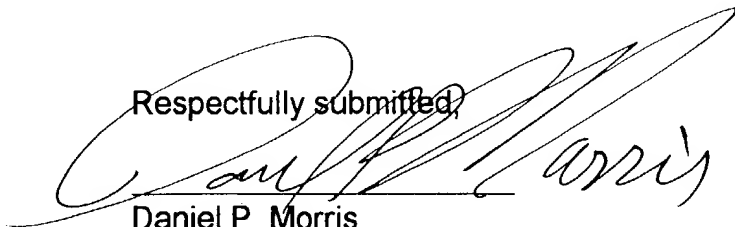
**LETTER**

Sir:

Attached is a SUBSTITUTE SUPPLEMENTAL APPELLANT'S REPLY TO THE EXAMINER'S ANSWER, text only, which corrects typographical errors in the SUPPLEMENTAL APPELLANT'S REPLY TO THE EXAMINER'S ANSWER submitted on August 4, 2000. The attachments can be found with the supplemental reply. Attachment A herein contains copies of the title page and table of contents of Ginsburg, D.M., Ed., Physical Properties of High-Temperature Superconductors, Vol. III, World Scientific, Singapore, 1989-1992, which is not included in Attachment E in the Supplemental Reply submitted on August 4, 2000, since it was not available at the time.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

Respectfully submitted,



Daniel P. Morris  
Reg. No. 32,053  
(914) 945-3217

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598  
Application Number: 08/303,561

Docket YO987-074BY

**ATTACHMENT A**

Application Number: 08/303,561

Docket YO987-074BY



# PHYSICAL PROPERTIES OF HIGH TEMPERATURE SUPERCONDUCTORS III

**Editor**

**Donald M. Ginsberg**

*Department of Physics  
University of Illinois at Urbana-Champaign*

 **World Scientific**  
*Singapore • New Jersey • London • Hong Kong*

*Published by*

World Scientific Publishing Co. Pte. Ltd.

P O Box 128, Farrer Road, Singapore 9128

USA office: Suite 1B, 1060 Main Street, River Edge, NJ 07661

UK office: 73 Lynton Mead, Totteridge, London N20 8DH

PHYSICAL PROPERTIES OF HIGH TEMPERATURE  
SUPERCONDUCTORS III

Copyright © 1992 by World Scientific Publishing Co. Pte. Ltd.

*All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the Publisher.*

ISBN 981-02-0874-X

ISBN 981-02-0875-8 (pbk)

Printed in Singapore by Utopia Press.

*With the de*

*to his famil*

*Joli, A*

*to his high-*

*B. G.*

*J. Gio*

*to his high-*

*E. D.*

*to the ma*

*to his*

*high-*

*and to his*

*A. C*

*S. L*

*M. B*

*M. L*

## CONTENTS

Preface	vii
Chapter 1. Fabrication and Characterization of Single Crystals of High Temperature Superconductors <i>S. E. Stupp and D. M. Ginsberg</i>	1
Chapter 2. The Influence of High Pressure on the Superconducting and Normal Properties of High Temperature Superconductors <i>J. S. Schilling and S. Klotz</i>	59
Chapter 3. Thermal Conductivity of High-Temperature Superconductors <i>C. Uher</i>	159
Chapter 4. Transport Properties of High $T_c$ Cuprates <i>Y. Iye</i>	285
Chapter 5. Optical Properties of High-Temperature Superconductors <i>D. B. Tanner and T. Timusk</i>	363
Chapter 6. Films of High-Temperature Oxide Superconductors <i>T. R. Lemberger</i>	471
Chapter 7. Tunneling Spectroscopy of Oxide Superconductors <i>T. Hasegawa, H. Ikuta and K. Kitazawa</i>	525
Subject Index	623
Appendix	629



MR. MANNY W. SCHECTER  
IBM CORPORATION  
INTELLECTUAL PROPERTY LAW DEPT.  
P.O. BOX 218  
YORKTOWN HEIGHTS, NEW YORK 10598

<sup>3 copies</sup>  
FILING SECOND SUPPLEMENTAL APPELLANT'S REPLY TO THE EXAMINER'S  
ANSWER, AND 5 BOOKS AS REFERENCES IN THE SECOND SUPPLEMENTAL  
APPELLANT'S REPLY TO THE EXAMINER'S ANSWER.

PLEASE STAMP & RETURN TO US

RECEIVED

OCT 10 2000

in re application of: J. G. Bednorz et al.

For: TECHNOLOGY CENTER 1700

Serial No.: 08/303,561 ; Docket No.: Y0987-074BY Atty.: DPM

Received in the U.S. Patent & Trademark Office

No. of pages of specification : No. of pages of claims

No. of sheets of drawings:

Declaration is attached to specification.

All fees are charged to our Account No. 09-0469

**BEFORE THE BOARD OF PATENT APPEALS  
AND INTERFERENCES**

Paper No. 93

Application Number: 08/303,561

Filing Date: September 09, 1994

Applicants: Johannes G. Bednorz et al.

Examiner M. Kopec

Daniel P. Morris  
For Appellant

**SECOND SUPPLEMENTAL APPELLANT'S REPLY  
TO THE EXAMINER'S ANSWER**

Appellant's SUBSTITUTE SUPPLEMENTAL APPELLANT'S REPLY TO THE EXAMINER'S ANSWER TEXT ONLY, submitted on August 24, 2000, refers to Attachment C that contains a Table 1 of high T<sub>c</sub> materials from the "CRC Handbook of Chemistry and Physics" 2000-2001 Edition. Table 1 lists 7 references as the source of the information on the 42 high T<sub>c</sub> materials in Table 1. Those references are listed below. Attachments E to K of the Appellant's SUBSTITUTE SUPPLEMENTAL APPELLANT'S REPLY TO THE EXAMINER'S ANSWER TEXT ONLY, submitted on August 24, 2000, contain the title page and table of contents of the books corresponding to references 1-5 respectively. References 6 and 7 are articles, copies of which were in Attachments J and K, respectively, of Appellant's SUBSTITUTE

SUPPLEMENTAL APPELLANT'S REPLY TO THE EXAMINER'S ANSWER TEXT ONLY, submitted on August 24, 2000. Enclosed are the books corresponding to Attachments E (Vols. I and II), F, H and I. The books corresponding to Attachment E (Vol. III) and Attachment G will not be available until late November 2000. They will be submitted to the USPTO when they are received by appellants.

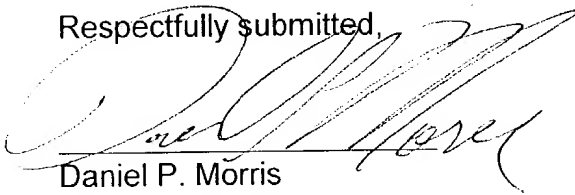
1. Attachment E  
Ginsburg, D.M., Ed., Physical Properties of High-Temperature Superconductors, Vols. I-III, World Scientific, Singapore, 1989-1992.
2. Attachment F  
Rao, C.N.R., Ed., Chemistry of High-Temperature Superconductors, World Scientific, Singapore, 1991.
3. Attachment G  
Shackelford, J.F., The CRC Materials Science and Engineering Handbook, CRC Press, Boca Raton, 1992, 98-99 and 122-123.
4. Attachment H  
Kaldis, E., Ed., Materials and Crystallographic Aspects of HTc-Superconductivity, Kluwer Academic Publ., Dordrecht, The Netherlands, 1992.
5. Attachment I  
Malik, S.K. and Shah, S.S., Ed., Physical and Material Properties of High Temperature Superconductors, Nova Science Publ., Commack, N.Y., 1994.
6. Attachment J  
Chmaissem, O. et al., Physica C230, 231-238, 1994
7. Attachment K  
Antipov E. V. et al., Physica C215, 1-10, 1993, 231-238, 1994

The is no evidence in these references that the 42 high Tc materials of Attachment C cannot be made following appellants' teaching.

Appellants request the Board to reverse the examiners rejections of claims under 35 USC 112, first paragraph.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

Respectfully submitted,

A handwritten signature in cursive script, appearing to read "Daniel P. Morris", is written over a horizontal line.

Daniel P. Morris  
Reg. No. 32,053  
(914) 945-3217

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598

	DATE	TIME	TO/FROM	MODE	MIN/SEC	PGS	CMD#	STATUS
17	09/30	10:38	917033086199	EC--S	00'46"	002	227	OK

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Appellant: J. Bednorz et al.

Date: September 30, 2002

Application No.: 08/303,561

Group Art Unit: 1751

Appeal No.: 2001-0809

Examiner: M. Kopec

Filed: 09/09/94

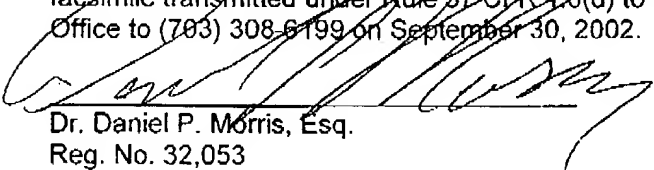
Docket No.: YO987-074BY

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

Assistant Commissioner for Patents  
Washington, D.C. 20231

**CERTIFICATE OF FACSIMILE TRANSMISSION**

I hereby certify that this paper (1 page) and executed Confirmation (1 page) are being facsimile transmitted under Rule 37 CFR 1.8(d) to the U.S. Patent and Trademark Office to (703) 308-6199 on September 30, 2002.

  
Dr. Daniel P. Morris, Esq.  
Reg. No. 32,053

**CONFIRMATION OF ATTENDANCE AT ORAL HEARING**

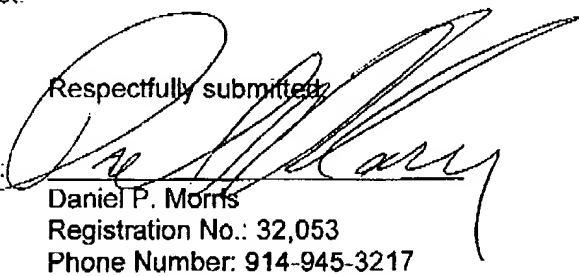
Sir:

In the Request For Oral Hearing dated June 28, 1999, Applicants requested one hour for the oral hearing. Applicants renew that request. Applicants request that an overhead transparency projector be available for use at the oral hearing.

Please charge deposit account no. 09-0468 the fee under 37 CFR 1.17(g) and any other fee necessary to enter this request.

Respectfully submitted,

By:

  
Daniel P. Morris  
Registration No.: 32,053  
Phone Number: 914-945-3217

IBM Corporation  
Intellectual Property Law Department  
P.O. Box 218  
Yorktown Heights, New York 10598



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appellant: J. Bednorz et al.

Date: September 30, 2002

Application No.: 08/303,561

Group Art Unit: 1751

Appeal No.: 2001-0809

Examiner: M. Kopec

Filed: 09/09/94

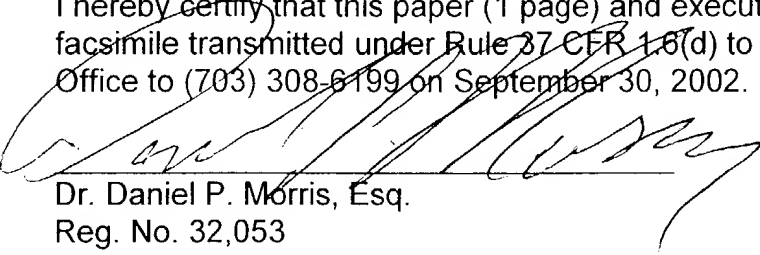
Docket No.: YO987-074BY

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

Assistant Commissioner for Patents  
Washington, D.C. 20231

**CERTIFICATE OF FACSIMILE TRANSMISSION**

I hereby certify that this paper (1 page) and executed Confirmation (1 page) are being facsimile transmitted under Rule 37 CFR 1.6(d) to the U.S. Patent and Trademark Office to (703) 308-6199 on September 30, 2002.

  
Dr. Daniel P. Morris, Esq.  
Reg. No. 32,053

**CONFIRMATION OF ATTENDANCE AT ORAL HEARING**

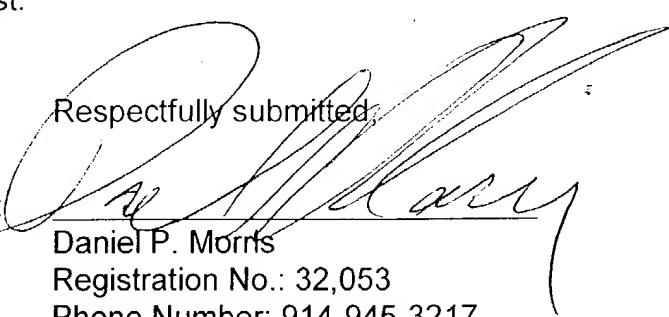
Sir:

In the Request For Oral Hearing dated June 28, 1999, Applicants requested one hour for the oral hearing. Applicants renew that request. Applicants request that an overhead transparency projector be available for use at the oral hearing.

Please charge deposit account no. 09-0468 the fee under 37 CFR 1.17(g) and any other fee necessary to enter this request.

Respectfully submitted,

By:

  
Daniel P. Morris  
Registration No.: 32,053  
Phone Number: 914-945-3217

IBM Corporation  
Intellectual Property Law Department  
P.O. Box 218  
Yorktown Heights, New York 10598

MAILED

SEP 17 2002



UNITED STATES DEPARTMENT OF COMMERCE  
Patent and Trademark Office

ASSISTANT SECRETARY AND COMMISSIONER OF  
PATENTS AND TRADEMARKS  
Washington, D.C. 20231

YOR9-1987-0074US4

2296 PAT. & T.M. OFFICE  
BOARD OF PATENT APPEALS  
AND INTERFERENCES

Daniel P. Morris  
IBM Corporation  
Intellectual Property Law  
Department  
P.O. Box 218  
Yorktown Heights, NY 10598

Appeal No:  
Appellant:  
Application No:  
Hearing Room:  
Hearing Docket:  
Hearing Date:  
Hearing Time:  
Location:

Paper No: 98  
2001-0809  
Bednorz, Johannes et. al.  
08/303,561  
A  
A  
Wednesday, November 06, 2002  
1:00 PM  
Room 12C07  
CRYSTAL GATEWAY 2  
1225 Jefferson Davis Highway  
Arlington, VA 22202

NOTICE OF HEARING

CONFIRMATION REQUIRED WITHIN TWENTY-ONE DAYS

Due 10/8/02

Your attention is directed to 37 CFR § 1.194(a).

The above identified appeal will be heard by the Board of Patent Appeals and Interferences on the date indicated. Hearings will commence at the time set and as soon as the argument in one appeal is concluded, the succeeding appeal will be taken up.

The time allowed for argument is twenty minutes unless additional time is requested and permitted before the argument is commenced.

CONFIRMATION OR WAIVER OF THE HEARING IS REQUIRED.

This form must be completed below and filed with the Board of Patent Appeals and Interferences preferably by facsimile within TWENTY-ONE (21) DAYS from the mailing date of this notice indicating confirmation or waiver of the hearing. A copy of this form may alternatively be filed by mail if facsimile is not available.

Failure to file this form within this time period will be construed as a waiver of the request for oral hearing.

37 CFR § 1.136(a) does not apply.

By order of the Board of Patent Appeals and Interferences

BPAI HEARINGS FAX No:

(703) 308-6199

See 1108 Off. Gaz. Pat. Trademark  
Office 15 (Nov. 14, 1989)

BPAI Mailing Address:

BOARD OF PATENT APPEALS AND INTERFERENCES  
COMMISSIONER OF PATENTS AND TRADEMARKS  
WASHINGTON, D.C. 20231

Clerk of the Board (703)-308-9797

In all communications relating to this appeal, please identify the appeal by its number.

CHECK ONE:

- ☒ HEARING ATTENDANCE CONFIRMED  
☐ HEARING ATTENDANCE WAIVED

Signature of Attorney/Agent/Appellant

Date

Registration No.

*[Handwritten Signature]*

Sept. 25, 2002

32053

PLEASE TYPE OR PRINT FIRMLY - Last part is your Package Label

**From:**  
**IBM**  
Shipping Label  
Set

**80471**

Name of Originator (Please Print or Type) <b>JENNIFER A SMITH</b>		Tie Line	
Dept. # / Proj. # to be charged <b>G2WD/G2WP</b>	External Phone # <b>914 - 945 -3861</b>	<b>8 - 862</b>	
<b>IBM T.J. Watson Research Center</b>			
<input checked="" type="checkbox"/> Route 134 Yorktown Heights, NY 10598	<input type="checkbox"/> 30 Sawmill River Road Hawthorne, NY 10532		
To: <b>JOY DOYLE, INTELLECTUAL PROPERTY LAW DEPT.</b>			
Company Name <b>IBM CORPORATION</b>		Bldg./Office Location <b>SUITE 605</b>	
Street Address (P.O. Box Not Acceptable) <b>1735 JEFFERSON DAVIS HIGHWAY</b>			
City <b>ARLINGTON</b>	State <b>VA</b>	Zip Code <b>22202-3592</b>	
Telephone <b>(703) 412-2420</b>			

No. of Pkgs. <b>1</b>
--------------------------

Does This Shipment Contain Any Chemicals? Yes ☐ No ☒

Authorized Name <b>JENNIFER A SMITH</b>	Authorized Signature <i>Jennifer A. Smith</i>	Date Sent <b>8-3-2000</b>
--	--	------------------------------

Contents Description

Weight (If known)	Class <input checked="" type="checkbox"/> Printed Matter <input type="checkbox"/> Tapes <input type="checkbox"/> Electronic Parts
Dollar Value (If known)	<input type="checkbox"/> Other (Describe)

Special Instructions

Arrival Date Required <b>August 4, 2000</b>	Other
--	-------

Information Below To Be Completed By Shipping Department

First Carrier <b>Airborne</b>	Second Carrier
Bill of Lading	Bill of Lading
Date of Shipment	Date of Shipment

990-0463-3 (7/94 TF002)

ORIGINATOR 2

FILING SUPPLEMENTAL APPELLANT'S REPLY TO THE EXAMINER'S ANSWER  
WITH ATTACHMENTS A TO K AND 2 COPIES.

HAND DELIVERED.

PLEASE STAMP & RETURN TO US

In re application of: BEDNORZ ET AL.

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION...

Serial No.: 08/303,561; Docket No.: Y0987-074BY Atty.: DPM

Received in the U.S. Patent & Trademark Office: \_\_\_\_\_

No. of pages of specification: \_\_\_\_\_: No. of pages of claims: \_\_\_\_\_

No. of sheets of drawings: \_\_\_\_\_

Declaration is attached to specification.

All fees are charged to our Account No. 09-0468

00-IBM YORKTOWN

	DATE	TIME	TO/FROM	MODE	MIN/SEC	PGS	CMD#	STATUS
25	11/01	09:55	+97033086199	EC--S	00'30"	006	111	OK

---

# IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of: J. Bednorz et al.

Date: November 1, 2002

Serial No: 08/303,561

Group Art Unit: 1751

Filed: 09/09/94

Examiner: M. Kopec

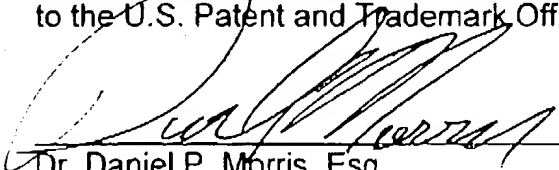
For: NEW SUPERCONDUCTIVE COMPOUNDS  
HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION

Docket No.: YO987-074BY

Assistant Commissioner for Patents  
Washington, D. C. 20231

## CERTIFICATE OF FACSIMILE TRANSMISSION

I hereby certify that this paper is being facsimile transmitted under Rule 37 CFR 1.6(d) to the U.S. Patent and Trademark Office to (703) 308-6199 on November 1, 2002.

  
Dr. Daniel P. Morris, Esq.  
Reg. No. 32,053

## TRANSMITTAL LETTER

Attn.: Craig R. Fienberg

Enclosed herewith is a copy of Appellants' Answer hand delivered on October 10, 2000. Appellants have misplaced the copy of this paper in their hard copy file. The enclosed copy has been made from Appellants' soft copy in their computer files. Enclosed is copy of the return postcard indicating that this paper was received by the USPTO on October 10, 2000.

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of: J. Bedniorz et al.

Date: November 1, 2002

Serial No: 08/303,561

Group Art Unit: 1751

Filed: 09/09/94

Examiner: M. Kopec

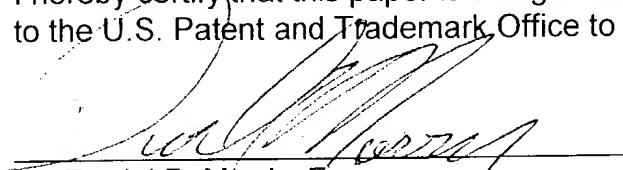
For: NEW SUPERCONDUCTIVE COMPOUNDS  
HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION

Docket No.: YO987-074BY

Assistant Commissioner for Patents  
Washington, D. C. 20231

**CERTIFICATE OF FACSIMILE TRANSMISSION**

I hereby certify that this paper is being facsimile transmitted under Rule 37 CFR 1.6(d) to the U.S. Patent and Trademark Office to (703) 308-6199 on November 1, 2002.



Dr. Daniel P. Morris, Esq.  
Reg. No. 32,053

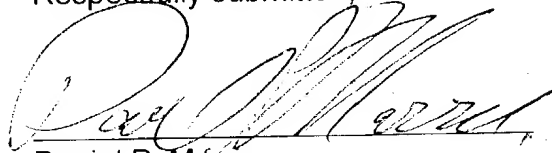
**TRANSMITTAL LETTER**

Attn.: Craig R. Fienberg

Enclosed herewith is a copy of Appellants' Answer hand delivered on October 10, 2000. Appellants have misplaced the copy of this paper in their hard copy file. The enclosed copy has been made from Appellants' soft copy in their computer files. Enclosed is copy of the return postcard indicating that this paper was received by the USPTO on October 10, 2000.

Please charge deposit account no. 09-0468 the fee under 37 CFR 1.17(g) and any other fee necessary to enter this request.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Daniel P. Morris", written over a horizontal line.

By: Daniel P. Morris  
Registration No.: 32,053  
Phone Number: 914-945-3217

IBM Corporation  
Intellectual Property Law Department  
P.O. Box 218  
Yorktown Heights, New York 10598

**BEFORE THE BOARD OF PATENT APPEALS  
AND INTERFERENCES**

Paper No. 92

Application Number: 08/303,561

Filing Date: September 09, 1994

Applicants: Johannes G. Bednorz et al.

Examiner M. Kopec

Daniel P. Morris  
For Appellant

**SUPPLEMENTAL  
APPELLANT'S REPLY TO THE EXAMINER'S ANSWER**

In the appellants' reply reference was made to the article "Synthesis of Cuprate Superconductors" by Rao et al., IOP Publishing Ltd. 1993. A copy of this article is in Attachment C to the reply brief. This article lists in Table 1 the properties of 29 cuprate superconductors made according to appellants teaching. Twelve (#'s 1, 8-13, 16, 17, 20, 21, 27 and 28) of those listed do not come within the scope of the claims allowed by the examiner. Only three of the 29 have a  $T_c < 26^\circ\text{K}$ . Those twelve do not contain one or more of a rare earth, a group IIIB element or an alkaline earth element. It is thus clear that broader claims than allowed in the answer should be allowed since it is clear that the allowed claims can be avoided following appellants teaching without undue experimentation.

The article of Rao et al. in the first sentence of the introduction citing appellants' article - which is incorporated by reference in their application - acknowledges that appellants initiated the field of high Tc superconductivity. Appellants further note that the Rao article acknowledges that "a large variety of oxides" are prepared by the general principles of ceramic science and that appellants discovered that metal oxides are high Tc superconductors.

Citing reference 5 therein - the book "New Directions in Solid State Chemistry", Rao et al. 1989 (Cambridge; Cambridge University Press) for which there is a 1986 edition which predates appellants filing date Rao (See Attachment B) - Rao et al. states:

Several methods of synthesis have been employed for preparing cuprates, with the objective of obtaining pure monophasic products with good superconducting characteristics [3, 4]. The most common method of synthesis of cuprate superconductors is the traditional ceramic method which has been employed for the preparation of a large variety of oxide materials [5]. Although the ceramic method has yielded many of the cuprates with satisfactory characteristics, different synthetic strategies have become necessary in order to control factors such as the cation composition, oxygen stoichiometry, cation oxidation states and carrier concentration. Specifically noteworthy amongst these methods are chemical or solution routes which permit better mixing of the constituent cations in order to reduce the diffusion distance in the solid state [5, 6].



Such methods include coprecipitation, use of precursors, the sol-gel method and the use of alkali fluxes. The combustion method or self-propagating high-temperature synthesis (SHS) has also been employed.

Reference 5 is another example of a reference to the general principles of ceramic science incorporated into appellants teaching. The Rao et al. article states that the 29 materials reported on in the article and fabricated in Table 1 are fabricated using the general principles of ceramic science. Moreover, the Rao article states that these materials are fabricated by what the Rao article calls the "ceramic method" which is the preferred embodiment in appellants specification, yet 12 of the 29 materials in Table 1 do not come within the scope of the claims allowed by the examiner in the answer. Thus known examples fabricated according to appellants' teaching will not be literally infringed by the Rao, Duncombe and Poole examples.

Attachment A is the table of contents and Chapter 3 entitled "Preparative Strategies" of the 1989 edition of the book "New Directions in Solid State Chemistry", Rao et al. 1989 (Cambridge; Cambridge University Press). Attachment A is the table of contents and Chapter 3 entitled "Preparative Strategies" of the 1986 edition. Chapter 3 in each edition is substantially the same. Since the publication date of the 1986 edition is before appellants filing date, all 29 of the high Tc material in table 1 of the Rao article are made according to the general principals of ceramic science as taught by appellants.

Attachment C is a Table of high Tic materials from the "CRUCE Handbook of Chemistry and Physics" 2000-2001 Edition. Attachment D is a copy of this table with hand written numbers to the left of the materials. There are a total of 42 materials listed in Table 1 of which 21 (those marked with an asterisk in the table in Attachment D #s 1, 7-13, 16-18, 20, 21, 27, 28, 30, 31 and 41-44) do not contain one or more of a rare earth, a group III element or an alkaline earth element. Yet all 42 are made according to the general principals or ceramic science taught by appellants. Two of the 42 materials have a Tic of 25 K. Thus a person of skill in the art following appellants' teaching can fabricate materials which avoid the claims allowed by the examiner but not the claims not allowed by the examiner.

Table 1 in attachment C list 7 references as the source of the information on the 42 high Tic materials. Those references are listed below. For references 1-5 Attachments ELI, respectively contain the title page and table of contents of the corresponding book. References 6 and 7 are article, copies of which are in Attachments J and K respectively.

1. Attachment E  
Ginsburg, D.M., Ed., Physical Properties of High-Temperature Superconductors, Vols. I-III, World Scientific, Singapore, 1989-1992.
2. Attachment F  
Rao, C.N.R., Ed., Chemistry of High-Temperature Superconductors, World Scientific, Singapore, 1991.
3. Attachment G  
Shackelford, J.F., The CRC Materials Science and Engineering Handbook, CRC Press, Boca Raton, 1992, 98-99 and 122-123.
4. Attachment H

Kaldis, E., Ed., Materials and Crystallographic Aspects of HTc-Superconductivity,  
Kluwer Academic Publ., Dordrecht, The Netherlands, 1992.

5. Attachment I

Malik, S.K. and Shah, S.S., Ed., Physical and Material Properties of High Temperature  
Superconductors, Nova Science Publ., Commack, N.Y., 1994.

6. Attachment J

Chmaissem, O. et al., Physica C230, 231-238, 1994

7. Attachment K

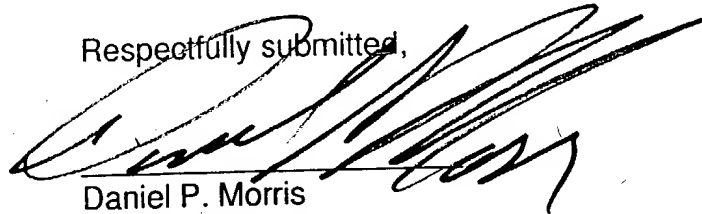
Antipov E. V. et al., Physica C215, 1-10, 1993. 231-238, 1994

The is no evidence in these references that the 42 high Tc materials of  
Attachment C cannot be made following appellants' teaching.

Appellants request the Board to reverse the examiners rejections of claims under  
35 USC 112, first paragraph.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

Respectfully submitted,



Daniel P. Morris  
Reg. No. 32,053  
(914) 945-3217

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598

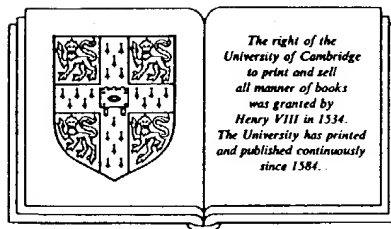
**ATTACHMENT A**

C. N. R. RAO, FRS  
J. GOPALAKRISHNAN

*Solid State and Structural Chemistry Unit, Indian Institute of Science,  
Bangalore, India*

## New directions in solid state chemistry

Structure, synthesis, properties, reactivity  
and materials design



CAMBRIDGE UNIVERSITY PRESS

Cambridge

New York Port Chester

Melbourne Sydney

Published by the Press Syndicate of the University of Cambridge  
 The Pitt Building, Trumpington Street, Cambridge CB2 1XP  
 40 West 20th Street, New York, NY 10011, USA  
 10 Stamford Road, Oakleigh, Melbourne 3166, Australia

© Cambridge University Press 1986

First published 1986

First paperback edition 1989

Printed in Great Britain at the University Press, Cambridge

*British Library cataloguing in publication data*

Rao, C. N. R.

New directions in solid state chemistry: structure,  
 synthesis, properties reactivity and materials design.-  
 (Cambridge solid state science series)

1. Solid state chemistry  
 I. Title II. Gopalakrishnan, J.  
 541'.0421 QD478

*Library of Congress cataloguing in publication data*

Rao, C. N. R. (Chintamani Nagesa Ramachandra), 1934-  
 New directions in solid state chemistry.

(Cambridge solid state science series)

Includes bibliographical references.

1. Solid state chemistry. I. Gopalakrishnan,  
 J. (Jagannatha), 1939- II. Title. III. Series.  
 QD478.R36 1986 541'.0421 85-22329

ISBN 0 521 30192 0 hard covers

ISBN 0 521 37935 0 paperback

## Contents

### Preface

ix

### 1 Structure of solids: old and new facets

#### 1.1 Introduction

1

#### 1.2 Description of crystals

1

#### 1.3 Bonding in crystals

2

#### 1.4 Inorganic structures

4

#### 1.5 Silicates and aluminosilicates

13

#### 1.6 Nonbonded interactions in ionic crystals

34

#### 1.7 New ways of looking at the structures of inorganic solids

39

#### 1.8 Polypisim

42

#### 1.9 Organic crystal structures

50

#### 1.10 Inclusion compounds and clathrates

53

#### 1.11 Noncrystalline or amorphous solids

56

#### 1.12 Quasicrystals

60

#### 1.13 Models and graphics

65

#### 1.14 Solitons

65

### 2 New and improved methods of characterization

67

#### 2.1 Introduction

67

#### 2.2 Structural characterization

68

##### 2.2.1 X-ray diffraction

70

##### 2.2.2 Electron diffraction

71

##### 2.2.3 Neutron diffraction and related techniques

73

##### 2.2.4 Electron microscopy

75

##### 2.2.5 X-ray absorption spectroscopy (EXAFS and XANES)

84

##### 2.2.6 Nuclear magnetic resonance spectroscopy (MASNMR)

95

##### 2.2.7 Electron spectroscopies

99

##### 2.2.8 Other spectroscopic techniques

105

##### 2.2.9 Concluding remarks

106

#### 2.3 Characterization of composition and purity

107

### 3 Preparative strategies

112

#### 3.1 Introduction

112

#### 3.2 Preparation of crystalline materials

116

##### 3.2.1 Ceramic methods

116

3.2.2. Chemical methods	118
3.2.3. High pressure methods	124
3.2.4. Arc techniques	130
3.2.5. Skull melting	132
3.2.6. Chemical vapour deposition (CVD)	132
3.2.7. Synthesis of organic solids	133
3.3. Microcrystalline particles and clusters (the finite solid state)	136
3.4. Amorphous materials	137
3.5. Crystal growth	139
<b>4 Phase transitions</b>	<b>148</b>
4.1. Introduction	148
4.2. Thermodynamics	148
4.3. Soft modes	153
4.4. Central peaks	156
4.5. Critical phenomena	157
4.6. Structural changes in phase transitions	158
4.7. Mechanisms of phase transitions	161
4.8. Organic solids	164
4.9. Incommensurate phases	166
4.10. Cooperative Jahn-Teller effect	176
4.11. Spin-state transitions	181
4.12. The plastic crystalline state	190
4.13. The liquid crystalline state	195
4.14. Noncrystalline state and the glass transition	200
4.15. Monte Carlo and molecular dynamics methods	204
4.16. Applications of phase transitions	206

5.5.4. Fluorite-related solids	237
5.6. Crystallographic shear	240
5.7. Block structures	244
5.8. Infinitely adaptive structures	247
5.9. Intergrowths	248
5.10. Defect perovskite oxides: a case study	252
<b>6 Structure-property relations</b>	<b>264</b>
6.1. Introduction	264
6.2. Electrons in solids	264
6.2.1. Band model	265
6.2.2. Localized electron model	268
6.2.3. Chemical bond approach	269
6.3. Properties	272
6.3.1. Magnetic properties	273
6.3.2. Electrical properties	284
6.3.3. Superconductivity	289
6.3.4. Dielectric and optical properties	292
6.4. Case studies	297
6.4.1. Metal oxides	297
6.4.2. Metal sulphides	311
6.4.3. Metal fluorides	320
6.5. Metal-nonmetal transitions	327
6.6. Metal clusters	339
6.7. Mixed-valence compounds	342
6.8. Low-dimensional solids	351
6.9. Ferroics	359
6.10. Liquid crystals	372
<b>7 Fashioning solids for specific purposes: aspects of materials design</b>	<b>377</b>
7.1. Introduction	377
7.2. Fast ion conductors	378
7.3. Photoelectrochemistry	386
7.4. Magnetic materials	394
7.5. Hydrogen storage materials	399
7.6. Amorphous materials	405
7.7. Organic materials	409
7.8. Langmuir-Blodgett films	413
7.9. Liquid crystals	413
7.10. Nonlinear optical materials	416
7.11. Luminescent inorganic materials	418

7.12	Laser materials	419
8	Reactivity of solids	421
8.1	Introduction	421
8.2	Nature of solid state reactions	421
8.3	Reactions involving a single solid phase	422
8.4	Solid-gas reactions	426
8.5	Solid-solid reactions	430
8.6	Solid-liquid reactions	434
8.7	Intercalation chemistry	434
8.8	Reactions of organic solids	449
8.9	Heterogeneous catalysis	460
9	Chemistry of high-temperature oxide superconductors	475
9.1	Introduction	475
9.2	Cuprates of $K_2NiF_4$ structure	476
9.3	Defect perovskites in the La-Ba-Cu-O system	477
9.4	$YBa_2Cu_3O_7$ and related 123 oxides	478
9.5	The $Ln_{1-x}Ba_{1+x}Cu_3O_{7+\delta}$ system	484
9.6	Bismuth and thallium cuprates	485
9.7	Nature of copper and oxygen in the superconducting cuprates	487
9.8	Preparative and related aspects	488
9.9	Concluding remarks	489
	References	491
	Index	521

## Preface

Although solid state science is an area of intense research activity pursued by physicists and materials scientists, the contributions of chemists to this area have a distinct identity. The great skill of chemists in developing novel methods for the synthesis of complex materials, and their understanding of the intricacies of structure and bonding, make their contributions to solid state science unique. At the present time, solid state chemistry is mainly concerned with the development of new methods of synthesis, new ways of identifying and characterizing materials and of describing their structure and above all, with new strategies for tailor-making materials with desired and controllable properties be they electronic, magnetic, dielectric, optical, adsorptive or catalytic. It is heartening that solid state chemistry is increasingly coming to be recognized as an emerging area of chemical science.

In this monograph, we have attempted to present the highlights of modern solid state chemistry and indicate the new directions in a concise manner. In doing so, we have not described the varied principles, properties and techniques that embody this subject at length, but have concerned ourselves with the more important task of bringing out the flavour of the subject to show how it works. We believe that the material covered is up to date, taking the reader to the very frontiers of the subject. We have been careful to include some introductory material for each aspect in order to enable students and beginners to benefit from the book. Instead of dividing the book into the traditional chapters (dealing with crystal chemistry, properties of solids, reactivity and so on) we have tried to present the subject in a style that would reflect the way the subject is growing today. Because of this approach, the lengths of the different chapters have inevitably become somewhat variable.

We hope that the book will be found useful by practitioners of solid state science, especially chemists interested in the study of condensed matter. While the book can certainly be used as a supplementary text in a broad course on solid state science, it could form the basis of a well-planned course in solid state chemistry. We shall be more than rewarded if the book is found useful by students, teachers and practitioners of solid state chemistry.

We have cited important material from the very recent literature including some of the latest references, but in dealing with some of the



### 3 Preparative strategies

#### 3.1 Introduction

Availability of pure, well-characterized solid samples is crucial to all solid state studies. A knowledge of the various experimental methods available for the preparation of solids therefore becomes an important and integral part of solid state chemistry (Hagemuller, 1972; Honig & Rao, 1981). A brief reflection on the development of solid state science reveals that, in many cases, it is the synthesis of a novel compound that has triggered off a new line of research. Tables 3.1 and 3.2 provide a few examples to illustrate the point. To many solid state

Table 3.1 *Some early solid state preparations that have led to major developments.<sup>a</sup>*

Prototype	First reported by (year)	Subsequent development
InP	Thiel (1910)	III-V semiconductors
ZrO <sub>2</sub> (CaO)	Ruff (1929)	Solid electrolyte, oxygen sensor
Na $\beta$ -alumina	Stillwell (1926)	Solid electrolyte, Na-S battery
V <sub>3</sub> Si	Wallbaum (1939)	Al <sub>5</sub> high temperature superconductors
BaTiO <sub>3</sub>	Tammann (1925)	Ferroelectrics, ceramic capacitors
LiNbO <sub>3</sub>	Sie (1937)	Nonlinear optics
BaFe <sub>12</sub> O <sub>19</sub>	Adelskold Schrevelius (1938)	Ferrites, memory devices
LnNi <sub>5</sub> (Ln = rare earth)	Klemm (1943)	Strong magnets, hydrogen storage materials
Amorphous Si	König (1944)	Solar cells
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> :Sb <sup>3+</sup> , Mn <sup>2+</sup>	McKeag, Ranby Jenkins (1949)	Fluorescent lamp phosphor
ZnS/CdS	Kröger (1940)	Cathode ray tube phosphor

<sup>a</sup> Partly taken from the US Panel Report on New Materials published by Centre for Materials Research, Stanford University (1979).

scientists, preparation of solids may mean preparation of single crystals of elements or simple compounds (e.g. Si, Ge, III-V semiconductors, alkali halides, etc.) for a study of a specific property or for technical applications. Preparation of solids is, however, a much more general activity, particularly amenable to chemists. A variety of strategies are adopted to prepare solids and to grow crystals. Technological advances have enabled solid state chemists to employ a broad range of conditions for preparative purposes. Ultra-rapid quenching of materials from very high temperatures, irradiation heating by intense laser beams, melting of solids by electron-beam heating or by the skull method and use of high pressures have become common procedures. When noncrystalline solids are required, they are prepared by sputtering, quenching and a number of other methods. To meet the challenge of producing materials which have hitherto required high temperatures, advantage is often taken of simple chemical methods.

Four categories of preparation of solids can be distinguished: (i) preparation of a series of compounds in order to investigate a specific property, as exemplified by a series of perovskite oxides to examine their electrical properties or by a series of spinel ferrites to screen their magnetic properties; (ii) preparation of unknown members of a structurally related class of solids to extend (or extrapolate) structure-property relations, as exemplified by the synthesis of layered chalcogenides and their intercalates or new derivatives of TTF-TCNQ to study their superconductivity; (iii) synthesis of a new class of compounds (e.g. silons, (Si, Al)<sub>3</sub>(O, N)<sub>4</sub>, or doped polyacetylenes) and (iv)

Table 3.2. *Some recently synthesized materials of technological relevance.*

Silicon (Si, Al) <sub>3</sub> (O, N) <sub>4</sub>	High temperature ceramics
Sm <sub>0.4</sub> Y <sub>2.6</sub> Ga <sub>1.2</sub> Fe <sub>3.8</sub> O <sub>12</sub>	Bubble memory devices
M <sub>2</sub> Mo <sub>6</sub> Se <sub>8</sub> and related Chevrel phases	High field superconductors
LnRh <sub>2</sub> B <sub>4</sub> (Ln = rare earth)	Coeistence of superconductivity and magnetism
Aluminosilicates (including ZSM-5)	Catalysis (e.g. methanol-gasoline)
Pb <sub>2</sub> Ru <sub>2-x</sub> Pb <sub>x</sub> O <sub>7-y</sub>	Electrocatalyst (for use in oxygen electrodes)
Polyacetylene ( <i>n</i> - and <i>p</i> -type doping)	Solid state batteries
Diacylene polymers	Nonlinear optic materials (better than LiIO <sub>3</sub> )
Organic liquid crystals	Display devices

preparation of known solids of prescribed specifications (crystallinity, shape, purity, etc.) as in the case of crystals of Si, III-V compounds and alkali halides. Category (iii) is a challenge that chemists respond to.

An understanding of the crystal chemistry is of the essence in designing new materials possessing desired properties. It is only when we have the correct prescription of structure (in relation to the properties of interest) that we can start synthetic efforts. As discussed in Chapter 1, even in metal oxides alone, we have several structures such as perovskites, spinels, bronzes and pyrochlores; new families have been identified during characterization and structural elucidation of oxides. Accordingly, several of the homologous series of oxides (see Table 3.3) have been identified through X-ray crystallography or electron microscopy rather than by chemical analysis, the precise compositions often being identified by structural considerations. Preparative solid state chemistry becomes most rewarding when there is close interaction between preparation, characterization (including structure determination) and study of properties. In what follows, we shall discuss the methods of preparation of solids in various states of aggregation ranging from the amorphous and the microcrystalline states to polycrystalline powders and finally to single crystals.

It is helpful to make a distinction between the preparation of new

Table 3.3 Some homologous series of metal oxides.

$Ti_nO_{2n-1}$	$4 \leq n \leq 9$ or $16 < n < 36$
$Mo_nO_{3n-1}$	$8 \leq n \leq 12$
$W_nO_{3n-2}$	$n = 20, 24, 25$ , etc.
$Pt_nO_{2n-2}$	$n = 4, 7, 9, 10, 11$ and $12$
$Bi(WO_3)_n$	$n = 6, 8, 15$ , etc.
$Bi_2W_nO_{3n+3}$	$n = 1, 2$ and $3$
$La_nNi_nO_{3n-1}$	$n = 2$ and above
$La_nCo_nO_{3n-1}$	$n = 2$ and above
$(Bi_2O_2)[A_{n-1}B_nO_{3n+1}]$	$A = Ba, Bi$ , etc. $B = Ti, Nb, W, Fe, Cr$ $n = 1-8$
$A_{n+1}B_nO_{3n+1}$	$A = Sr, B = Ti$ $A = La, B = Ni$ $n = 1, 2, 3$ , etc.
$A_nB_nO_{3n+2}$	$A = Na, Ca$ $B = Nb$ $n^a = 4, 5, 6$ and $7$

<sup>a</sup>Between  $n = 4$  and  $4.5$ , a large number of coherent intergrowth phases with long periodicities are known in this system (Portier *et al.*, 1975).

solids and the preparation of solids by new methods. Preparation of a new solid need not necessarily involve a new method. A number of instances can be cited where preparation of new solids with novel structures and properties is achieved by routine procedures. Typical of them are  $Na_3Zr_2PSi_2O_{12}$  (NASICON),  $Na_{1+x}Al_{11}O_{17+x/2}$  ( $\beta$ -alumina),  $BaFe_{12}O_{19}$  and  $MMo_6S_8$  ( $M = Cu, Pb$  etc.) Chevrel phases. All these solids are prepared by the ordinary method of reacting readily available constituents at elevated temperatures (the *ceramic method*). In the last case, the reaction is carried out in closed ampoules for the obvious reasons, but in others even this precaution is unnecessary. The importance of such preparations lies not in the method, but in selecting the right constituents in the right proportion, bearing in mind the chemistry as well as the structure and properties desired in the new phase. This aspect is illustrated by the synthesis of  $Na_3Zr_2PSi_2O_{12}$ , a fast sodium ion conductor, where the composition was chosen keeping in mind the coordination preferences of the atoms involved, the stability of their oxidation states, the nature of the network that would be formed and whether the network would permit three-dimensional mobility of sodium ions (Goodenough *et al.*, 1976). Another example of innovative synthesis by design is the preparation of synthetic bone material for prosthetic application (Roy, 1977). Here the problem is not only the synthesis of the chemical compound constituting the human bone, viz. calcium hydroxyapatite, but also having it with the 100% connectivity and porosity of the natural bone. The synthesis could be accomplished because of two realizations: certain marine corals ( $CaCO_3$ ) possess the same porosity and connectivity as the human bone and the aragonite form of  $CaCO_3$  can be topotactically converted to calcium hydroxyapatite in a hydrothermal reaction. Thus, the reaction of marine corals with phosphoric acid under hydrothermal conditions produces synthetic bone material.

Synthesis of new solids is not always achieved by design. Preparative solid state chemistry has its share of serendipitous discovery of new materials. The discovery of  $NaMo_4O_6$ , the prototype of metal cluster chain compounds, is an example of this category (Torardi & McCarty, 1979). The discovery resulted from a most innocent experiment aimed at preparing  $NaZn_2Mo_3O_8$ , the sodium-analogue of the lithium-containing cluster compound,  $LiZn_2Mo_3O_8$ . For this purpose, a mixture of  $Na_2MoO_4$ ,  $ZnO$ ,  $MoO_3$  and  $Mo$  was sealed in a molybdenum tube and heated at 1370 K. The product turned out to be shiny needles of  $NaMo_4O_6$  instead of the expected  $NaZn_2Mo_3O_8$ . The crystal structure of  $NaMo_4O_6$  turned out to be one of the most unique

oxide structures, consisting of infinite chains of  $\text{Mo}_6$  octahedral clusters sharing opposite edges (Fig. 1.17).

### 3.2 Preparation of crystalline materials

#### 3.2.1 Ceramic methods

The most common method of preparing solids is by the reaction of the component materials at elevated temperatures. If all the components are solids, the method is called the *ceramic method*. If one of the constituents is volatile or sensitive to the atmosphere, the reaction is carried out in sealed evacuated capsules. Ternary oxides, sulphides, phosphides, etc. have been prepared by this method. A knowledge of the phase diagram is generally helpful in fixing the desired composition and conditions for synthesis. Some caution is necessary in deciding the choice of the container; platinum, silica and alumina containers are generally used for the synthesis of metal oxides, while graphite containers are suitable for sulphides and other chalcogenides as well as pnictides.

Ceramic preparations often require relatively high temperatures (up to 2300 K) which can generally be attained by resistance heating. Electric arc and skull techniques can give temperatures up to 3300 K while high power  $\text{CO}_2$  lasers can give temperatures up to 4300 K.

Ceramic methods suffer from several disadvantages: (i) When no melt is formed during the reaction, the entire reaction has to occur in the solid state, first by a phase boundary reaction at the points of contact between the components and later by diffusion of the constituents through the product phase. With the progress of the reaction, diffusion paths become longer and longer and the reaction rate slower and slower; the reaction can be speeded up to some extent by intermittent grinding between the heating cycles. (ii) There is no way of monitoring the progress of the reaction in a ceramic method. It is only by trial and error that one decides appropriate conditions that lead to the completion of the reaction. Because of this difficulty, one often ends up with mixtures of reactants and products by the ceramic technique. Separation of the desired product from such mixtures is difficult, if not impossible. (iii) Frequently, it becomes difficult to obtain a compositionally homogeneous product by a ceramic technique even where the reaction proceeds almost to completion.

Despite these limitations, ceramic techniques have been widely used for solid state synthesis. Mention must be made, among others, of the successful use of this technique for the synthesis of rare earth mono-

chalcogenides such as  $\text{SmS}$  and  $\text{SmSe}$ . The method (Jayaraman *et al.*, 1975) consists of heating the elements, first at lower temperatures (870–1170 K) in evacuated silica tubes; the contents are then homogenised, sealed in tantalum tubes and heated at  $\sim 2300$  K by passing a high current through the tube. Metal-rich halides of lanthanides and other early transition elements have been synthesized using tantalum containers (Corbett, 1980, 1981). Several halides and chalcogenides possessing condensed metal clusters have also been prepared by the ceramic method (Simon, 1981). Metal-rich suboxides of alkali metals have been prepared by reacting the metal with required amounts of oxygen until the gas is entirely absorbed ( $p < 10^{-5}$  torr) (Simon, 1975). Examples of such phases are  $\text{Rb}_6\text{O}$ ,  $\text{Rb}_9\text{O}_2$ ,  $\text{Cs}_{11}\text{O}_3$ ,  $\text{Cs}_3\text{O}$ ,  $\text{Cs}_4\text{O}$  and  $\text{Cs}_7\text{O}$ . Extreme air sensitivity and low temperatures of decomposition/melting render the preparation and investigation of the phases very difficult. These oxides are therefore investigated *in situ*.

Various modifications of the ceramic technique have been employed to overcome some of the limitations. One of these relates to decreasing the diffusion path lengths. In a polycrystalline mixture of reactants, the individual particles are of approximately  $10\text{ }\mu\text{m}$  size, which represents diffusion distances of roughly 10 000 unit cells. By using freeze-drying, spray-drying, coprecipitation and sol-gel and similar techniques, it is possible to bring down the particle size to a few hundred angstroms (see Section 3.3) and thus effect a more intimate mixing of the reactants. In *spray-drying*, suitable constituents dissolved in a solvent are sprayed in the form of fine droplets into a hot chamber. The solvent evaporates instantaneously leaving behind an intimate mixture of reactants, which on heating at elevated temperatures gives the product. In *freeze-drying*, the reactants in a common solvent are frozen by immersing in liquid nitrogen and the solvent removed at low pressures. In *coprecipitation*, the required metal cations are coprecipitated from a common medium, usually as hydroxides, carbonates, oxalates, formates or citrates, which are subsequently heated at appropriate temperatures to yield the final product. These methods have been used for the preparation of polycrystalline samples of several oxides such as ferrites, perovskites and  $\beta$ -aluminas. The *sol-gel process* (Johnson, 1981) involves forming a concentrated sol of the reactant oxides or hydroxides and converting it to a semirigid gel by removing the solvent. The solvent is removed by passing fine droplets of the sol through a column of an aliphatic alcohol (e.g. 2-ethyl-1-hexanol). The dehydrated gel is heated at an appropriate temperature to obtain the product. Several complex oxide materials such as  $\text{NASICON}$ ,  $\text{PbTi}_{1-x}\text{Zr}_x\text{O}_3$ ,  $\text{ThO}_2 - \text{UO}_2$  solid solutions and

Zr<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> modifications (Alamo & Roy, 1984) have been prepared by this method. The sol-gel technique has also become important for the preparation of noncrystalline solids (Schoize, 1984).

### 3.2.2 Chemical methods

There have been significant attempts to overcome the limitations of the ceramic method, resulting in alternative routes for solid state synthesis. The new methods, which rely on the knowledge of the structural chemistry and the reactivity patterns of solids, have not only enabled the synthesis of known solids in a state of high purity and homogeneity at far lower temperatures than by the conventional methods, but, in addition, have resulted in the synthesis of new phases. Among these alternative strategies, the following three methods have proved significant: the solid state precursor method and methods based on topochemical redox reactions and topochemical ion-exchange reactions. The emphasis in all three methods is in achieving the synthesis at low temperatures so that the products obtained are in a finely divided state with large surface areas – a feature essential for catalysis and other applications. More importantly, synthesis at temperatures considerably lower than the sintering temperatures of solids preserves the essential features of the parent structure with minimal structural reorganization (topochemical methods). Synthesis by topochemical methods often yields metastable phases that cannot be obtained by conventional methods.

The ideal condition for carrying out a solid state reaction in order to obtain a homogeneous product in the shortest time at the lowest possible temperature is to ensure homogeneous mixing of the reactants on an atomic scale. This, however, cannot be achieved in the ceramic method or its modifications. The only way to achieve this is to prepare a single phase (a chemical compound) in which the reactants are present in the required stoichiometry. Such a solid phase, called a *precursor*, on heating gives the desired product in a stoichiometric and homogeneous state. The *precursor method* has been employed for the synthesis of ternary oxides (Wold, 1980). Spinel-type ferrites, MFe<sub>2</sub>O<sub>4</sub> (M = Mg, Mn, Co, Ni), have been prepared by thermal decomposition of acetate precursors of the general formula M<sub>3</sub>Fe<sub>6</sub>(CH<sub>3</sub>COO)<sub>17</sub>O<sub>3</sub>OH.12C<sub>2</sub>H<sub>5</sub>N. The advantage of this method is that the precursors can be prepared as crystalline solids in a stage of high purity, possessing the desired M/Fe ratio. Moreover, the products are homogeneous and formed at fairly low temperatures. Other examples of synthesis of metal oxides through the compound precursor route are preparation of chromites, MCr<sub>2</sub>O<sub>4</sub>, by the decomposition of dichromates, (NH<sub>4</sub>)<sub>2</sub>M(CrO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, prepara-

tions of BaTiO<sub>3</sub> and LiCrO<sub>2</sub> by the decomposition of Ba[TiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>] and Li[Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] and of LaFeO<sub>3</sub> by the decomposition of La[Fe(CN)<sub>6</sub>]. Another example is the synthesis of ceramic oxides by the hydrolysis of metal alkoxides.

It is not always possible to find suitable single precursor compounds for the synthesis of all the desired compositions, because the stoichiometry of the precursor may not correspond to that of the product. Recently, a solid-solution precursor method which retains all the advantages of single compound precursors has been described (Horowitz & Longo, 1978; Longo & Horowitz, 1981; Vidyasagar *et al.*, 1984, 1985). The strategy is to make use of isostructural compounds containing a common anion so that they form a continuous series of solid solutions. The method has been used for the synthesis of several ternary oxides in the Ca–Mn–O system, such as Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>, CaMn<sub>3</sub>O<sub>6</sub>, CaMn<sub>4</sub>O<sub>8</sub> and CaMn<sub>5</sub>O<sub>12</sub> by the thermal decomposition of carbonate solid solutions, Ca<sub>1-x</sub>Mn<sub>x</sub>CO<sub>3</sub>, of calcite structure. Ca<sub>1-x</sub>Fe<sub>x</sub>CO<sub>3</sub> has been used to prepare unusual ferrites; Ca<sub>2</sub>Fe<sub>2-x</sub>Mn<sub>x</sub>O<sub>5</sub> with three types of transition metal–oxygen polyhedra have also been prepared in this manner. The method has been extended to hydroxide, oxalate and nitrate precursor solid solutions. Using hydroxides of the La(OH)<sub>3</sub> structure, compounds like LaNiO<sub>3</sub> and quaternary oxides have been prepared. Using nitrate precursors, BaPbO<sub>3</sub>, Ba<sub>2</sub>PbO<sub>4</sub> and BaSrPbO<sub>4</sub> have been prepared. Solid solution precursors have several advantages: (i) The reacting cations are uniformly blended together, thereby avoiding diffusion problems (the diffusion distance in this method is ~10 Å) and compositional inhomogeneities in the final product. (ii) The final product is formed at a much lower temperature than in a conventional ceramic synthesis, thus permitting an examination of subsolidus regions of the phase diagram which would otherwise be inaccessible. The products formed at lower temperatures will have large specific surface areas, which is an important requirement in catalyst preparations. The solid solution precursor method has been used for the low-temperature synthesis of Mo–W alloys (Cheetham, 1980) by hydrogen reduction of (NH<sub>4</sub>)<sub>6</sub>[Mo<sub>7-x</sub>W<sub>x</sub>O<sub>24</sub>].

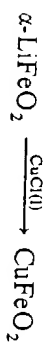
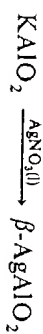
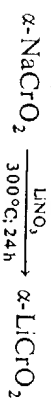
*Vapour phase decomposition* of precursors at relatively low temperatures has been employed to produce solids. Thus SiC is formed by the decomposition of CH<sub>3</sub>SiH<sub>3</sub> or (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub>, while Si<sub>3</sub>N<sub>4</sub> is produced by the reactive decomposition of SiCl<sub>4</sub> or SiH<sub>4</sub> and NH<sub>3</sub>. Silon powders are made by the reaction of metakaolin with NH<sub>3</sub> vapour. Transition metal sulphides are prepared by the reaction of precursor oxides, sulphates and chlorides with H<sub>2</sub>S or CS<sub>2</sub>. Pyrochlores of the type Pb<sub>2</sub>[Ru<sub>2-x</sub>Pb<sub>x</sub>]<sup>2+</sup>O<sub>7-y</sub> and Bi<sub>2</sub>[Ru<sub>2-x</sub>Bi<sub>x</sub>]<sup>3+</sup>O<sub>7-y</sub> are prepared by a

Table 3.4 Intercalation and deintercalation of lithium into  $MX_n$  hosts

$MX_n$ host	Remarks	References
$TiS_2$	$Li_xTiS_2$ ; $0 < x \leq 1$ . Phase is homogeneous over the composition $Li_xVS_2$ ; $0 < x \leq 1$ . Phases obtained by deintercalation of lithium from $LiVS_2$ using $I_2/CH_3CN$ . Three different phase regions:	Whittingham (1978) Murphy <i>et al.</i> (1977)
$VS_2$	$0.25 \leq x \leq 0.33$ ; $0.48 \leq x \leq 0.62$ and $0.85 \leq x \leq 1$ apart from $VS_2$	
$NbS_2(3R)$	$Li_{0.5}NbS_2$ and $Li_{0.70}NbS_2$	Whittingham (1978)
$TiS_3$	$Li_2TiS_3$ and $Li_{2+x}TiS_3$ ( $0 < x \leq 1$ )	Whittingham (1978)
$MoS_3$	$Li_xMoS_3$ ( $0 < x \leq 4$ )	Jacobson <i>et al.</i> (1979)
$MO_2$ (rutile)	$Li_xMO_2$ ( $x \geq 1$ ) ( $M = Mo, Ru, Os$ or $Ir$ )	Murphy <i>et al.</i> (1978)
$TiO_2$ (anatase)	$Li_xTiO_2$ ( $0 < x \leq 0.7$ ). $Li_{0.5}TiO_2$ transforms irreversibly to $LiTi_2O_4$ spinel at 500 °C	Murphy <i>et al.</i> (1982)
$CoO_2$	$Li_xCoO_2$ ( $0 < x < 1$ ). Phases obtained by electrochemical delithiation of $LiCoO_2$	Mizushima <i>et al.</i> (1980)
$VO_2$	$Li_xVO_2$ ( $0 < x < 1$ ): Phases obtained by chemical delithiation of $LiVO_2$ using $Br_2/CHCl_3$	Vidyasagar & Gopalakrishnan (1982)
$VO_2(B)$	$Li_xVO_2$ ( $0 < x < 2/3$ ): Chemical lithiation using $n$ -butyl lithium	Murphy & Christian (1979)
$Fe_2O_3$	$Li_xFe_2O_3$ ( $0 < x < 2$ ): Anion array transforms from hcp to ccp on lithiation	Thackeray <i>et al.</i> (1982)
$Fe_3O_4$	$Li_xFe_3O_4$ ( $0 < x < 2$ ): $Fe_2O_4$ subarray of the spinel structure remains intact	Thackeray <i>et al.</i> (1982)
$Mn_3O_4$	$Li_xMn_3O_4$ ( $0 < x < 1.2$ ): Lithium insertion suppresses tetragonal distortion of $Mn_3O_4$	Thackeray <i>et al.</i> (1983)
$MoO_3$	$Li_xMoO_3$ ( $0 < x < 1.55$ )	Dickens & Pye (1982)
$V_2O_5$	$Li_xV_2O_5$ ( $0 < x < 1.1$ ): Intercalation of lithium by using $LiI$	Dickens <i>et al.</i> (1979)
$ReO_3$	$Li_xReO_3$ ( $0 < x \leq 2$ ): Three phases $0 < x \leq 0.35$ ; $x = 1$ and $1.8 \leq x \leq 2$	Murphy <i>et al.</i> (1981) Cava <i>et al.</i> (1982)

both in aqueous and molten salt conditions. Thus, sodium  $\beta$ -alumina has been exchanged with  $H_3O^+$ ,  $NH_4^+$  and other monovalent and divalent cations, giving rise to different  $\beta$ -aluminas (Farrington & Briant, 1978; Tofield, 1982). *Ion-exchange* in inorganic solids is a general phenomenon, not restricted to fast ion conductors alone. The kinetic and thermodynamic aspects of ion-exchange in inorganic solids have been examined by England *et al.* (1983). Their results reveal that ion-exchange is quite a widespread phenomenon, occurring even when the diffusion coefficients are as small as  $\sim 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ , at temperatures far below the sintering temperatures of solids. Ion-exchange can occur at a considerable rate even in stoichiometric solids; mobile ion vacancies (introduced by nonstoichiometry or doping) are not required. Since the exchange occurs topochemically, it enables preparation of metastable phases that are inaccessible by high-temperature reactions.

England *et al.* (1983) have shown that a variety of metal oxides having layered, tunnel or close-packed structures can be ion-exchanged in aqueous solutions or molten salt media to produce new phases. Typical examples are:

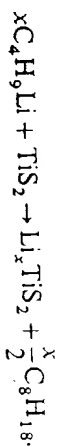


The structure of the framework is largely retained during the exchange except for minor changes to accommodate the structural preferences of the incoming ion. Thus, when  $\alpha\text{-LiFeO}_2$  is converted to  $\text{CuFeO}_2$  by exchange with molten  $\text{CuCl}$ , the structure changes from that of  $\alpha\text{-NaCrO}_2$  to that of delafossite to provide a linear anion coordination for  $\text{Cu}^+$ . Similarly when  $\text{KAlO}_2$  is converted to  $\beta\text{-AgAlO}_2$  by ion-exchange, there is a structure change from cristobalite-type to ordered wurtzite-type. The change probably occurs to provide a tetrahedral coordination for  $\text{Ag}^+$ . An interesting ion-exchange reaction reported by Rice & Jackel (1982) is the conversion of  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  to  $\text{HfNbO}_3$  and  $\text{HTaO}_3$ , respectively, by treatment with hot aqueous acid. The exchange of  $\text{Li}^+$  by protons is accompanied by a topotactic transformation of the rhombohedral  $\text{LiNbO}_3$  structure to the cubic perovskite structure of  $\text{HfNbO}_3$ . The mechanism suggested for the transformation is the reverse of the transformation of cubic  $\text{ReO}_3$  to rhombohedral  $\text{LiReO}_3$  and  $\text{Li}_x\text{ReO}_3$  (Cava *et al.*, 1982), involving a twisting of the octahedra along the [111] cubic direction so as to convert the 12-coordinated perovskite tunnel sites to two 6-coordinated sites in the rhombohedral structure. Another interesting structural change accompanied by ion-exchange is



low-temperature method employing strongly alkaline media (Horowitz *et al.*, 1981). The high-temperature phase ( $> 1300$  K) of  $\text{ZrO}_2$  is obtained at room temperature by the hydrolysis of zirconium salts. The cubic ( $\delta$ ) form of  $\text{Bi}_2\text{O}_3$  can be stabilized at room temperature by incorporating additives such as  $\text{Y}_2\text{O}_3$  and  $\text{WO}_3$ .  $\gamma\text{-Fe}_2\text{O}_3$  is obtained by the dehydration of  $\gamma\text{-FeOOH}$  by organic bases (Desiraju & Rao, 1982). *Fused salt electrolysis* (Banks & Wold, 1974) is employed to synthesize oxides such as blue Mo bronzes.

Transition metal oxides and chalcogenides,  $\text{MX}_n$  ( $M = \text{metal}$ ), possessing layered or chain structures can be intercalated at room temperature with lithium and other alkali metals to give the reduced phases,  $A_x\text{MX}_n$  ( $A = \text{Li, Na or K}$ ). Formation of such phases was first reported by Rüdorff (1959). The process has several features which make it attractive both as a preparative technique and for the application of the phases as battery cathodes (Murphy & Christian, 1979): (i) the reaction is reversible and can be brought about chemically or electrochemically; (ii) the reaction is topochemical in nature, occurring with minimal structural reorganization of the host,  $\text{MX}_n$ ; and (iii) A cations as well as electrons transferred to the host possess considerable mobility in  $A_x\text{MX}_n$  phases, rendering them mixed ionic-electronic conductors. It is this last feature that makes them useful as cathode materials in solid state batteries. The best known example of alkali metal intercalation is that of lithium into  $\text{TiS}_2$  to give  $\text{Li}_x\text{TiS}_2$  ( $0 < x \leq 1.0$ ) (Whittingham, 1978; Whittingham & Chianelli, 1980). The intercalation can be carried out by two methods. In the first, a chemical reagent, *n*-butyl lithium dissolved in a hydrocarbon solvent. Such as hexane, is employed as the lithiating agent:



The second method for synthesizing lithium intercalates involves electrochemical reduction of  $\text{TiS}_2$ . A polycrystalline sample of  $\text{TiS}_2$  bonded into an electrode form is immersed in a polar organic solvent (e.g. dioxolane) in which lithium chloride (VII) is dissolved. A sheet of lithium metal of LiAl serves as the anode. On shorting the two electrodes, lithium ions intercalate  $\text{TiS}_2$ , the charge-compensating electrons passing through the external circuit. Electrochemical intercalation is particularly advantageous because the rate of the reaction can be controlled by imposing an external voltage across the cell; when the voltage exceeds the value corresponding to the free energy change  $\Delta G$  of the intercalation reaction, the reverse reaction – namely deintercalation – occurs.

Intercalation of lithium has been achieved in a variety of  $\text{MX}_n$  hosts.

*Deintercalation* of lithium has also been done both electrochemically and chemically. Deintercalation of lithium from  $\text{LiMX}_n$  using mild oxidizing agents such as  $\text{I}_2/\text{CH}_3\text{CN}$  and  $\text{Br}_2/\text{CHCl}_3$  offers a low-temperature route for the synthesis of  $\text{Li}_x\text{MX}_n$  and  $\text{MX}_n$  phases that are otherwise impossible to prepare, such as  $\text{Li}_x\text{VS}_2$  and  $\text{Li}_x\text{VO}_2$ . Similarly  $\text{Mo}_6\text{S}_8$  can be prepared by acid leaching of  $\text{Cu}_x\text{Mo}_6\text{S}_8$  (Chevreil *et al.*, 1974). In Table 3.4 we list representative examples of lithium intercalation and deintercalation. From the table, it is seen that lithium intercalation occurs in a wide variety of oxide and sulphide hosts possessing one-, two-, and three-dimensional structures. In most cases, the gross structural features of the host are retained. In some cases, there are specific structural changes which can be accounted for within the framework of a topochemical mechanism, e.g.  $\text{LiReO}_3$  and  $\text{Li}_2\text{ReO}_3$  (Cava *et al.*, 1982). In both  $\text{LiReO}_3$  and  $\text{Li}_2\text{ReO}_3$ , the  $\text{ReO}_3$  host undergoes significant change on lithium insertion without breaking bonds. The 12-coordinated cavities in the  $\text{ReO}_3$  framework each become two octahedral cavities which are occupied by lithium. Lithium insertion in close-packed oxides such as  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Mn}_3\text{O}_4$  and  $\text{TiO}_2$  results in interesting structural changes. Lithium insertion changes the anion array of  $\text{Fe}_2\text{O}_3$  from hexagonal to cubic close packing. Lithium insertion suppresses the cooperative Jahn–Teller distortion of  $\text{Mn}_3\text{O}_4$ . Lithium-inserted anatase,  $\text{Li}_0.5\text{TiO}_2$ , transforms to the superconducting spinel  $\text{LiTi}_2\text{O}_4$  around 770 K. Deintercalation of lithium by electrochemical methods or with iodine from  $\text{Li}_2\text{FeS}_2$  leads reversibly to  $\text{LiFeS}_2$ , which has the  $\text{LiTiS}_2$  structure.

Intercalation of sodium and potassium differs from that of lithium. In layered  $A_x\text{MX}_n$ , lithium is always octahedrally coordinated, while sodium and potassium occupy octahedral or trigonal prismatic sites; octahedral coordination is favoured by large values of  $x$  and low formal oxidation states of  $M$ . For smaller  $x$  and larger oxidation states of  $M$ , the coordination of sodium or potassium is trigonal prismatic. Intercalated caesium in  $\text{MX}_n$  is always trigonal prismatic. Intercalation of sodium and potassium in layered  $\text{MX}_2$  oxides and sulphides results in structural transformations involving a change in the sequence of anion layer stacking.

A number of inorganic solids having layered or a three-dimensional network structure exhibit fast cation transport. Sodium  $\beta$ - and  $\beta'$ -aluminas are typical examples. Sodium ions in these solids move rapidly in layers which provide a number of empty sites and easy pathways for ionic motion. Diffusion coefficients are typically of the order of  $10^{-7}$   $\text{cm}^2\text{s}^{-1}$ . Fast cation conductors such as  $\beta$ -aluminas are good ion-exchangers. The exchange can be carried out easily at room temperature

reported in  $\text{Na}_{0.7}\text{CoO}_2$  by Delmas *et al.* (1982). In  $\text{Na}_{0.7}\text{CoO}_2$ , the anion layer sequence is ABBA; cobalt ions occur in alternate interlayer octahedral sites and sodium ions in trigonal prismatic coordination in between the  $\text{CoO}_2$  units. When this material is ion-exchanged with LiCl, a metastable form of  $\text{LiCoO}_2$  with the layer sequence ABCBA is obtained. The phase transforms irreversibly to the stable  $\text{LiCoO}_2$  (ABCABC) around 520 K.

A variety of inorganic solids has been exchanged with protons to give new phases, some of which exhibit high protonic conduction; typical of them are  $\text{HTaWO}_6 \cdot \text{H}_2\text{O}$  (Groult *et al.*, 1982),  $\text{HMO}_3 \cdot x\text{H}_2\text{O}$  ( $M = \text{Sb}$ , Nb, Ta) pyrochlores (Chowdhry *et al.*, 1982) and  $\text{HTiNbO}_6$  layer phase (Rebbah *et al.*, 1982). Ion-exchange has also been reported in metal sulphides. For example,  $\text{KFeS}_2$  undergoes topochemical exchange of potassium in aqueous solutions with alkaline earth metal cations to give new phases in which the  $[\text{FeS}_{4/2}]_{\infty}$  tetrahedral chain is preserved (Boller, 1978).

### 3.2.3 High pressure methods

The use of high pressure for solid state synthesis has acquired special significance after the synthesis of diamond by the General Electric Co. in 1955. Early investigations in this area were concerned with pressure-temperature phase diagrams of elements like Si, Ge and Bi. With the development of high-pressure technology, commercial equipment permitting simultaneous use of both high-pressure and high-temperature conditions have become available since the 1960s. Reviews presenting the experimental aspects and research progress in this area are available (Goodenough *et al.*, 1972; Joubert & Chenavas, 1975; Pistorius, 1976).

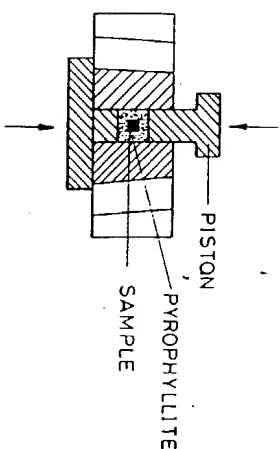
Experimental facilities required for high pressure synthesis may be divided into two major categories depending on the range of pressures involved. For the 1–10 kbar pressure range, the *hydrothermal method* is often employed. In this method, the reaction is carried out either in an open or a closed system. In the open system, the solid is in direct contact with the reacting gases ( $\text{F}_2$ ,  $\text{O}_2$  or  $\text{N}_2$ ) which also serve as pressure-intensifiers. Normally, a gold container is used in this type of synthesis. The method has been used for the synthesis of transition metal compounds such as  $\text{RhO}_2$ ,  $\text{PtO}_2$  and  $\text{Na}_2\text{NiF}_6$ , where the transition metal is in a high oxidation state. Hydrothermal high pressure synthesis under closed system conditions has also been used for the preparation of higher-valence metal oxides; here, an internal oxidant like  $\text{KClO}_3$  is added to the reactants, which on decomposition under reaction conditions provides the necessary oxygen pressure. For example, oxide pyrochlores of palladium(IV) and platinum(IV),  $\text{Ln}_2\text{M}_2\text{O}_n$ , have been

prepared by this method (970 K, 3 kbar). ( $\text{H}_3\text{O})\text{Zr}_2(\text{PO}_4)_3$  (Subramanian *et al.*, 1984) and a family of zero thermal expansion ceramics (e.g.  $\text{Ca}_{0.5}\text{Ti}_2\text{P}_3\text{O}_{12}$ ) (Roy *et al.*, 1984) have also been prepared hydrothermally.

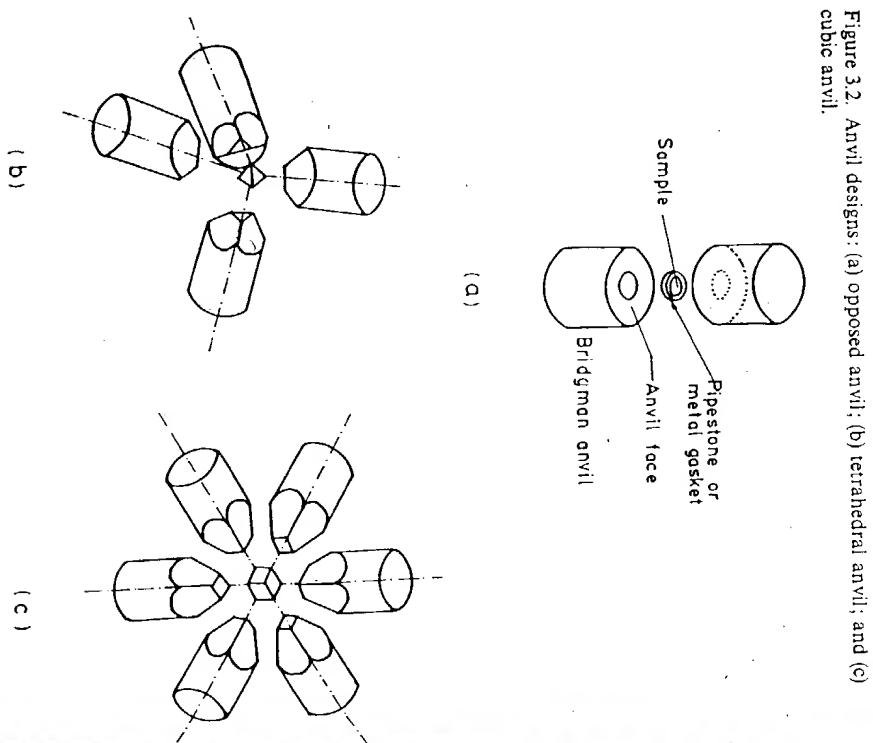
Zeolites are generally prepared under hydrothermal conditions in the presence of alkali (Barrer, 1981). The alkali, the source of silicon and the source of aluminium are mixed in appropriate proportions and heated (often below 370 K). A common reactant mixture is a hydrous gel composed of an alkali (alkali or alkaline earth metal hydroxide, organic quaternary bases, etc.), fresh  $\text{Al}(\text{OH})_3$  and silica sol or alkali, soluble aluminate, and silica sol. Under alkaline conditions, Al is present as  $\text{Al}(\text{OH})_4^-$  anions. The  $\text{OH}^-$  ions act as mineralizing catalyst while the cations present in the reactant mixture determine the kinds of zeolite formed. Besides water, some inorganic salts are also encapsulated in some zeolites. Zeolitization in the presence of organic bases has been developed and this route is useful for synthesizing silica-rich zeolites. Silicalite with a tetrahedral framework enclosing a three-dimensional system of channels (defined by 10 rings wide enough to absorb molecules up to 0.6 nm in diameter) has been synthesized by the reaction of tetrapropylammonium (TPA) hydroxide and a reactive form of silica between 370 and 470 K. The precursor crystals have the composition  $(\text{TPA})_2\text{O}_{.48}\text{SiO}_2 \cdot \text{H}_2\text{O}$  and the organic cation is removed by chemical reaction or thermal decomposition to yield microporous silicalite which may be considered to be a new polymorph of  $\text{SiO}_2$  (Flanigen *et al.*, 1978). The clathrasil (silica analogue of a gas hydrate), dodecasil-1H, is prepared from an aqueous solution of tetramethoxysilane and  $\text{N}(\text{CH}_3)_4\text{OH}$ ; after the addition of aminoadamantane, the solution is treated hydrothermally under nitrogen for four days at 470 K (Groenen *et al.*, 1983).

Pressures in the range 10–150 kbar are commonly used for solid-state synthesis and such pressures are attained with three different kinds of apparatus: (i) In the *piston-cylinder apparatus* (Fig. 3.1), consisting of a

Figure 3.1. Piston-cylinder apparatus.



tungsten carbide chamber and a piston assembly, the sample is contained in a suitable metal capsule surrounded by a pressure-transducer (pyrophyllite). Pressure is generated by moving the piston through the blind hole in the cylinder. An internal microfurnace made of graphite or molybdenum can be incorporated in the design. Pressures up to 50 kbar and temperatures up to 1800 K are readily reached in a volume of 0.1 cm<sup>3</sup> using this design. (ii) In the *anvil apparatus* (Fig. 3.2), first designed by Bridgman, the sample is subjected to pressure by simply squeezing it between two opposed anvils. Massive support to the anvils is provided by the surrounding rings. Although pressures of  $\sim 200$  kbar and temperatures up to 1300 K can be reached in this technique, it is not popular for solid-state synthesis since only milligram quantities can be handled. An extension of the opposed anvil principle is the tetrahedral

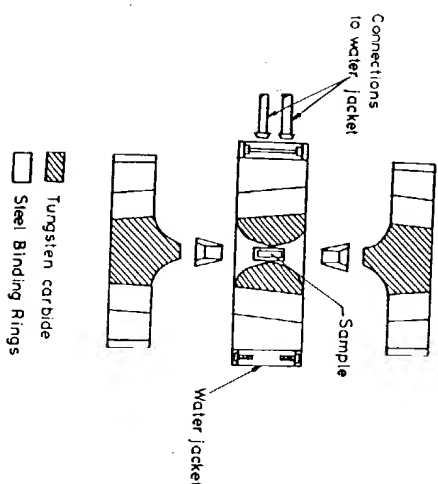


anvil design, where four massively supported anvils disposed tetrahedrally ram towards the centre where the sample is located in a pyrophyllite medium together with a heating arrangement. The multi-anvil design has been extended to cubic geometry, where six anvils act on the faces of a pyrophyllite cube located at the centre. (iii) The *'belt' apparatus* (Fig. 3.3) provides probably the most successful high pressure-high temperature combination for solid-state synthesis. This apparatus, which has been used for the synthesis of diamonds in the US is in a way a combination of the piston-cylinder and the opposed anvil designs; massive support is provided to the anvil as well as the cylinder. The apparatus consists of two conical pistons made of tungsten carbide, which ram through a specially shaped chamber from opposite directions. The chamber and pistons are laterally supported by several steel rings making it possible routinely to reach fairly high pressures ( $\sim 150$  kbar) and high temperatures ( $\sim 2300$  K).

In the 'belt' apparatus, the sample is contained in a noble metal capsule (a BN or MgO container is used for chalcogenides) and surrounded by pyrophyllite and a graphite sleeve, the latter serving as an internal heater. In a typical high-pressure run, the sample is loaded, the pressure raised to the desired value and then the temperature increased. After holding the pressure for about 30 minutes, the sample is quenched ( $400 \text{ K s}^{-1}$ ) while still under pressure. The pressure is then released after the sample has cooled to room temperature.

High-pressure research requires suitable calibration and measurement of pressures. Calibration is carried out by making use of standard

Figure 3.3. The belt apparatus.





substances which are known to undergo structure transitions at definite pressures.

Solids generally undergo transformations at high pressures to more close-packed structures, with an increase in coordination number. For example, on application of pressure, Si and Ge transform from a four- to a six-coordinated (white tin) structure, iron transforms from an eight- to a twelve-coordinated structure, while NaCl goes to the CsCl structure. The simple rule that high pressures result in lower volume and higher coordination number is based on the hard sphere model, which assumes constant radius and compressibility for atoms in different structures. The only generalization we can make is that pressure-induced transitions proceed in the direction of greater packing efficiency; less efficiently packed structures have a greater probability of undergoing pressure-induced structural changes. Pressure-induced phase transitions of solids may be quenchable or nonquenchable. Many high pressure forms of solids can be retained under ambient conditions as metastable phases, a typical case being that of diamond (quenchable). In general, transformations belonging to the reconstructive type, involving breaking and making of bonds, can be quenched; transformations involving only a slight movement of atoms are difficult to quench. This is the case with the monoclinic-tetragonal transition of  $\text{ZrO}_2$ , as also the tetragonal (red  $\text{PbO}$  type)-wurtzite transition of  $\text{SnO}$ . A large class of materials having quenchable high-pressure phases is the class of perovskite-related polytypes of  $\text{ABX}_3$  ( $\text{X} = \text{F}, \text{O}$ ) compositions (Goodenough *et al.*, 1972). In these cases, pressure has the effect of decreasing the tolerance factor,  $t$ , and hence stabilizing the cubic close-packing of the  $\text{AX}_3$  layers (B ion octahedra share corners) as against hexagonal close-packing (B ion octahedra share faces). In transition metal hydroxides,  $\text{MOOH}$ , the normal-pressure boehmite structure gives way to diasporite and  $\text{InOOH}$ -type structures at high pressures.

High-pressure methods have been used for the synthesis of new solids that cannot possibly be made otherwise. In general, the formation of a new compound from its components requires that the new composition has a lower free energy than the sum of the free energies of the components. Pressure can aid in the lowering of free energy in different ways (Goodenough *et al.*, 1972): (i) Pressure can delocalize outer  $d$  electrons in transition-metal compounds by increasing the magnitude of coupling between the  $d$  electrons on neighbouring cations, thereby lowering the free energy. Typical examples are provided by the synthesis of  $\text{ACrO}_3$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{Pb}$ ) perovskites and  $\text{CrO}_2$ . (ii) Pressure can stabilize higher-valence states of transition metals, thus promoting the formation of a new phase. For instance, in the  $\text{Ca-Fe-O}$  system only  $\text{CaFeO}_2$ ,

(brownmillerite) is stable under ambient pressures. Under high oxygen pressures, iron is oxidized to the  $4^+$  state and hence  $\text{CaFeO}_3$  with the perovskite structure is formed. (iii) Pressure can suppress the ferroelectric displacement of cations and this aids the synthesis of new phases. The synthesis of  $\text{A}_x\text{MoO}_3$  bronzes, for example, requires populating the empty  $d$  orbitals centred on molybdenum; at ambient pressures,  $\text{MoO}_3$  is stabilized by a ferroelectric distortion of  $\text{MoO}_6$  octahedra up to the melting point. (iv) Pressure can alter site-preference energies of cations, thus facilitating the formation of new phases. For example, it is not possible to synthesize  $\text{A}^{2+}\text{Mn}^{4+}\text{O}_3$  ( $\text{A} = \text{Mg}, \text{Co}, \text{Zn}$ ) ilmenites because of the strong tetrahedral site preference of the divalent cations and one obtains a mixture of  $\text{A}[\text{A}(\text{Mn})\text{O}_4(\text{spinel}) + \text{MnO}_2(\text{rutile})]$  under atmospheric pressure instead of a single phase  $\text{AMnO}_3$ . However, the latter is formed at high pressures with a corundum-type structure in which both A and Mn ions are in octahedral coordination. (v) Pressure can suppress the  $6s^2$  core polarization in oxides containing  $\text{Tl}^+, \text{Pb}^{2+}, \text{Bi}^{3+}$  isoelectronic cations. For example, a perovskite-type  $\text{PbSnO}_3$  cannot be made at atmospheric pressure because a mixture of  $\text{PbO} + \text{SnO}_2$  is more stable than a perovskite.

Stabilization of unusual oxidation states and spin states of transition metals is of considerable interest (e.g.  $\text{La}_2\text{Pd}_2\text{O}_7$ ). Such stabilization can be rationalized by making use of correlations of structural factors with the electronic configuration. Six-coordinated high-spin iron(IV) has been stabilized in  $\text{La}_{1-x}\text{Sr}_x\text{Li}_{0.5}\text{Fe}_{0.5}\text{O}_4$ , which has the  $\text{K}_2\text{NiF}_4$  structure (Demazeau *et al.*, 1982a). The elongated  $\text{FeO}_6$  octahedra and the presence of ionic  $\text{Li-O}$  bonds resulting from the  $\text{K}_2\text{NiF}_4$  structure favour the high-spin  $\text{Fe(IV)}$  state. The Li and Fe ions in this oxide are ordered in the  $ab$ -plane as evidenced by supercell spots in the electron diffraction pattern. Such an oxide is prepared under oxidizing conditions.  $\text{CaFeO}_3$  and  $\text{SrFeO}_3$  prepared under oxygen pressure also contain octahedral  $\text{Fe(IV)}$ ; while  $\text{Fe(IV)}$  in  $\text{SrFeO}_3$  is in the high-spin state with the  $e_g$  electron in the narrow  $\sigma^*$  band down to 4K,  $\text{Fe(IV)}$  in  $\text{CaFeO}_3$  disproportionates to  $\text{Fe(III)}$  and  $\text{Fe(V)}$  below 290 K (Takano & Takeda, 1983).  $\text{La}_2\text{LiFeO}_6$  prepared under high oxygen pressure has the perovskite structure with the iron in the pentavalent state (Demazeau *et al.*, 1982a).

Nickel in the 3+ state is present in the perovskite  $\text{LaNiO}_3$ , which can be prepared at atmospheric pressure; other rare earth nickelates can, however, be prepared at high oxygen pressures.  $\text{La}_2\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}_4$  and  $\text{MLaNiO}_4$  ( $\text{M} = \text{Sr}$  or  $\text{Ba}$ ) with the  $\text{K}_2\text{NiF}_4$  structure are other examples of oxides with  $\text{Ni(III)}$  (Demazeau *et al.*, 1982b).  $\text{MNiO}_{3-x}$  ( $\text{M} = \text{Ba}$  or  $\text{Sr}$ ) prepared under high pressure contain  $\text{Ni(IV)}$  as well (Takeda *et al.*,

1976). In  $\text{La}_2\text{Li}_0.5\text{Co}_0.5\text{O}_4$ , there is evidence for the transformation of the low-spin  $\text{Co(II)}$  to the intermediate- as well as high-spin states. The Li and Co ions are ordered in the *ab*-plane of this oxide of  $\text{K}_2\text{NiF}_4$  structure; the highly elongated  $\text{CoO}_6$  octahedra seem to stabilize the intermediate-spin state (Mohanram *et al.*, 1983). Intermediate-spin Co ions are reported to be formed in  $\text{Sr}_4\text{TaCoO}_8$  and  $\text{Sr}_4\text{NbCoO}_8$  as well. Oxides in perovskite and  $\text{K}_2\text{NiF}_4$  structures with trivalent Cu have been prepared under high oxygen pressure (Demazeau *et al.*, 1982b). High  $\text{F}_2$  pressure has been employed to prepare  $\text{Cs}_2\text{NiF}_6$  and other fluorides (Hagemuller, 1985).

As noted earlier, solid state reactions are generally slow under ordinary pressures even when the product is thermodynamically stable. Pressure has a marked effect on the kinetics of the reaction, reducing the reaction times considerably and at the same time resulting in more homogeneous and crystalline products. For instance,  $\text{LnFeO}_3$ ,  $\text{LnRhO}_3$  and  $\text{LnNiO}_3$  ( $\text{Ln}$  = rare earth) are prepared in a matter of hours at high pressure – high temperature conditions, whereas under ambient pressures the reactions require several days ( $\text{LnFeO}_3$  and  $\text{LnRhO}_3$ ) or they do not occur at all ( $\text{LnNiO}_3$ ). In several  $(\text{AX})(\text{ABX}_3)_n$  series of compounds, the end members  $\text{ABX}_3$  and  $\text{A}_2\text{BX}_4$ , having the perovskite and  $\text{K}_2\text{NiF}_4$  structures respectively, are formed at atmospheric pressures but not the intermediate phases such as  $\text{A}_3\text{B}_2\text{X}_7$  and  $\text{A}_4\text{B}_3\text{X}_{10}$ . Pressure facilitates synthesis; for instance,  $\text{Sr}_3\text{Ru}_2\text{O}_7$  and  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$  are formed in 15 min at 20 kbar and 1300 K.  $\text{TaS}_3$ ,  $\text{NbSe}_3$  and such solids are prepared in 30 min at 2 GPa and 970 K.

### 3.2.4 Arc techniques

Use of the electric arc for the preparation of materials as well as growth of crystals of refractory solids has been reviewed by Loehman *et al.* (1969) and Müller-Buschbaum (1981). Basically, an arc for synthetic purposes is produced by passing a high current from a tungsten cathode to a crucible anode which acts as the container for the material to be synthesized (Fig. 3.4). The cathode tip is ground to a point in order to sustain a high current density. Typical operating conditions involve currents of the order of 70 amp at 15 volts. The arc is maintained in inert ( $\text{He}$ ,  $\text{Ar}$ ,  $\text{N}_2$ ) or reducing ( $\text{H}_2$ ) atmospheres. Even traces of oxygen attack the tungsten electrode and therefore the gases are freed from oxygen (by gettering with heated titanium sponge) before passing into the arc chamber. The arc can be maintained in an oxygen atmosphere using graphite electrodes instead of tungsten. The crucible (anode) is made from a cylindrical copper block and is water-cooled during operation. For the synthesis of materials, the starting materials are placed in the copper crucible. An arc is struck by allowing the cathode to touch the

anode. The current is raised slowly while the cathode is simultaneously withdrawn so as to maintain the arc. The arc is then positioned so that it bathes the sample in the crucible. The current is increased until the reactants melt. When the arc is turned off, the product solidifies in the form of a button. Because of the enormous temperature gradient between the melt and the water-cooled crucible, a thin solid layer of the sample usually separates the melt from the copper hearth; in this sense, the sample forms its own crucible and hence contamination with copper does not take place. Contamination of the sample by tungsten vaporizing from the cathode can be avoided by using water-cooled cathodes. The arc method has been successfully used for the synthesis of various oxides of Ti, V and Nb. A number of lower-valence rare earth oxides,  $\text{LnO}_{1.5-x}$ , have been prepared by arc fusion of  $\text{Ln}_2\text{O}_3$  with Ln metal.

A sophisticated version of the arc method is the *triarc technique* (Fig. 3.4) developed by Fan & Reed (1972) for growing single crystals of high-melting solids. The main differences between the single and triarc furnace lie in the use of three symmetrically arranged thoriated tungsten cathodes and a graphite crucible as anode, together with a water-cooled pulling rod. For crystal growth using the triarc furnace, the polycrystalline sample is loaded in the crucible, all the three arcs are struck simultaneously and the sample is brought to just-melting condition. The pulling rod is then lowered down until the tip just touches the melt. By slowly pulling the rod up, a 'neck' is formed between the frozen solid and the melt in the crucible. This is equivalent to using a single seed crystal in the conventional pulling technique for crystal growth. Careful driving of

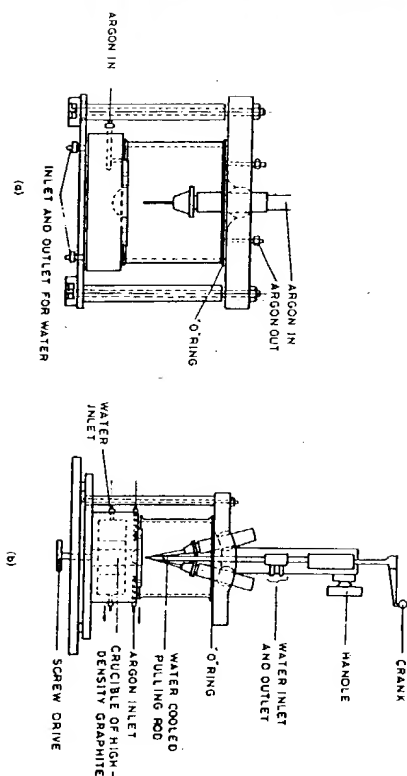


Figure 3.4. (a) D.C. arc furnace; (b) Triarc.

the pulling rod while maintaining the triarc produces a single crystal boule. The method has been used to grow single crystals of  $\text{Ti}_3\text{O}_5$ ,  $\text{Ti}_2\text{O}_3$  and  $\text{NbO}$ .

A further modification of the arc method is the *arc transport (transfer) technique* in which the material to be grown as a single crystal is transported by an electric arc. A vertical arc between the cathode (filled with the melt) and the anode carrying the seed crystal is kept at constant length by progressively raising the anode. The fused material is transported across the arc from cathode to anode where it grows on the seed crystal. NiO crystals have been prepared by this technique by using Ni electrodes (Honig & Rao, 1981).

### 3.2.5 *Skull melting*

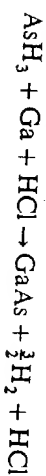
This technique is useful not only for preparing metal oxides, but also for growing crystals of these oxides. The technique involves coupling of the material to a radio frequency electromagnetic field (200 kHz–4 MHz, 20–50 kW) (Harrison *et al.*, 1980). The material is placed in a container consisting of a set of water-cooled cold fingers set in a water-cooled base (all made of copper), the space between the fingers being large enough to permit penetration of the electromagnetic field into the interior, but small enough to avoid leakage of the melt. The process is crucibleless and a thin solid skull separates the melt from the water-cooled container. Single crystals of very large sizes can be grown by this method and the mass of the starting materials can be up to 1 kg. Temperatures up to 3600 K are reached in this technique, permitting growth of crystals of materials like  $\text{ThO}_2$  and stabilized  $\text{ZrO}_2$ . The stoichiometry of the oxide is readily controlled by the use of an appropriate ambient gas ( $\text{CO}/\text{CO}_2$  mixtures, air or oxygen). Large crystals of  $\text{CoO}$ ,  $\text{MnO}$  and  $\text{Fe}_3\text{O}_4$  have been grown by the skull method and the technique will undoubtedly find many applications in the future. In  $\text{CoO}$  and  $\text{MnO}$ , trivalent metal ions were eliminated by heating the crystals in an appropriate  $\text{CO}/\text{CO}_2$  mixture. Recently, crystals of  $\text{La}_2\text{NiO}_4$  and  $\text{Nd}_2\text{NiO}_4$  have been grown by the skull method.

### 3.2.6 *Chemical vapour deposition (CVD)*

Deposition of a solid on a substrate by means of a chemical reaction between vapours is called chemical vapour deposition (CVD). The process involves (i) the formation of reactants in the vapour state, (ii) transport of the vapour to the deposition region and (iii) deposition of the solid from the vapour. CVD has become an important technique in solid-state synthesis and finds application in the synthesis of a broad spectrum of solids ranging from amorphous and polycrystalline deposits

to epitaxial growth of single-crystal films used in devices (Tietjen, 1973). As a synthetic technique, CVD has several advantages. The method permits preparation of virtually any material in almost any geometry. Since product formation is not limited by kinetic factors and diffusion, it is possible to synthesize solids at relatively low temperatures; homogeneity and stoichiometry are also easily controlled. An additional advantage is that incorporation of selected dopants in controlled concentration during the synthesis is achieved.

CVD is widely used for the preparation of silicon and III–V semiconductors for device purposes. There are two different CVD processes for the preparation of silicon: (i) hydrogen reduction of  $\text{SiCl}_4$  and (ii) pyrolysis of  $\text{SiH}_4$ . The deposition is carried out either homoeopitaxially on silicon or on an insulating substrate such as sapphire. Several methods have been developed for the synthesis of III–V compounds. For example, GaAs is made by CVD using  $\text{AsCl}_3$  and Ga vapour in a hydrogen atmosphere; here,  $\text{AsCl}_3$  acts not only as the source of As but as the transporting agent for Ga as well. Another method for the synthesis of this class of compounds makes use of the reaction between a volatile hydride of a group V element with a group III element in the presence of HCl gas:



A third method makes use of hydrides of group V elements together with volatile organometallic compounds of group III elements such as trimethylgallium and trimethylaluminium.

Insulating materials such as  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$  and  $\text{Al}_2\text{O}_3$  have also been made by CVD methods.  $\text{Si}_3\text{N}_4$ , a high-temperature ceramic, is formed by the reaction of  $\text{NH}_3$  with  $\text{SiH}_4$  or  $\text{SiCl}_4$ . The reaction using  $\text{SiH}_4$  has the advantage that it occurs at lower temperatures. CVD has been particularly useful in the synthesis of superconducting and magnetic materials. One such material  $\text{Nb}_3\text{Si}$  is an important A15 superconductor. Preparation of this phase by the reaction of the elements at elevated temperatures yields only a nonsuperconducting phase which has the  $\text{Ti}_3\text{P}$  structure. It is only by deposition from vapours below 1120 K that the desired phase with the A15 structure is obtained. Rare earth garnets, useful as bubble-domain magnetic materials, have been prepared as single crystals by deposition from volatile metal halides.

### 3.2.7 *Synthesis of organic solids*

Synthesis is the main preoccupation of organic chemists and we can not possibly deal with the varied aspects of organic synthesis

here. Synthesis of organic solids exhibiting properties of interest to the solid state scientists however involves certain procedures which are noteworthy and we shall discuss a few typical systems of current interest. TTF-TCNQ and such donor-acceptor complexes and polyacetylene and other conducting organic polymers are areas of active study in solid state science today (Hatfield, 1979). Synthetic methods for the preparation of TTF, TCNQ and related donor and acceptor molecules are described in the literature (Narita & Pittman, 1976; Wheland & Martin, 1975). The charge transfer salts are usually prepared by mixing hot acetonitrile solutions of the donor and the acceptor. What is important for solid state chemistry is not the synthesis *per se* of these organic compounds, but the design of donors and acceptors so that the charge transfer solids possess the desired structure and properties. Certain guidelines based on molecular stacking, stoichiometry and degree of charge transfer have been evolved for the design of donor-acceptor complexes exhibiting metallic properties (Torrance, 1979). Thus, 1:1 charge transfer salts possessing uniform segregated stacking and incomplete charge transfer show metallic properties. There have been attempts to link the three factors to the molecular properties of donors and acceptors. Segregated stacking seems to be favoured when the donor-acceptor overlap is particularly weak. The degree of charge transfer is chiefly determined by the ionization energy of the donor (reduction potential of the cation). A plot of the room-temperature conductivity against the reduction potential of cation for the TCNQ family of donor-acceptor solids reveals that only in the narrow region of the reduction potential close to zero are the solids metallic. When the potential is too negative, complete charge transfer occurs giving ionic salts and when the potential is positive, neutral complexes are obtained (Torrance, 1979). Factors that determine the stoichiometry of donor-acceptor complexes are not definitely known. In the family of TTF-halide salts, the observed nonstoichiometries have been accounted for in terms of Madelung energy, showing that ionization potential of the donor and electron affinity of the acceptor are important factors determining stoichiometry.

Attempts have also been made to design one-dimensional organic superconductors based on donor-acceptor interaction (Bechgaard & Jerome, 1982). For this purpose it is necessary to avoid Peierls distortion, which results in the loss of metallic property (see Section 6.8). This is accomplished by preparing charge transfer complexes of selenium analogues of TTF such as TMTSF (Tetramethyltetraselenafulvalene). Charge transfer solids of the type TMTSF<sub>2</sub>X (X = ClO<sub>4</sub>, ReO<sub>4</sub>, PF<sub>6</sub> and AsF<sub>6</sub>) indeed show superconductivity, the perchlorate salt showing the

superconducting transition at 1.2 K and atmospheric pressure and the others at high pressures.

Polyacetylene, (CH)<sub>x</sub>, is the prototype of conducting organic polymers (Etemad *et al.*, 1982) whose electrical conductivity can be varied by doping over twelve orders of magnitude from that of an insulator ( $< 10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$ ) through semiconductor to a metal ( $> 10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$ ). Polyacetylene can be prepared by admitting acetylene gas into a glass reactor vessel whose inside wall has been wetted with a methylbenzene solution of (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Al and (n-C<sub>4</sub>H<sub>9</sub>O)<sub>4</sub>Ti Ziegler catalyst (Shirakawa & Ikeda, 1971; Shirakawa *et al.*, 1973). A cohesive film of polyacetylene grows on all surfaces which have been wetted by the catalyst solution. Polymerization at room temperature produces a mixture of 80% *cis* and 20% *trans* isomers. When the temperature is around 350 K, nearly 100% *cis*-(CH)<sub>x</sub> is produced; at 420 K (decane solvent) the product is 100% *trans*. The *cis-trans* isomerization occurs at  $\sim 470 \text{ K}$ . As formed, (CH)<sub>x</sub> films consist of randomly oriented fibrils, each fibril being a few hundred angstroms in diameter. The room-temperature conductivity of (CH)<sub>x</sub> depends upon the *cis* and *trans* content, the value varying between  $10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$  for the *cis* polymer ( $E_g \sim 0.8 \text{ eV}$ ) and  $10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$  for the *trans* polymer ( $E_g \sim 1.0 \text{ eV}$ ). As a result of the large overall band width arising from the conjugated  $\pi$ -electrons, (CH)<sub>x</sub> is different from the common organic semiconductors made up of weakly interacting molecules (e.g. anthracene) or from saturated polymers with no  $\pi$ -electrons (e.g. polyethylene).

Like inorganic semiconductors, polyacetylene can be doped with a variety of donors and acceptors to give *n*-type or *p*-type semiconductors. Doping to high levels (above  $\sim 1\%$ ) results in a semiconductor-metal transition giving a new class of metals with a wide range of electro-negativity (MacDiarmid & Heeger, 1979; Mammone & MacDiarmid, 1984). Doping can be done chemically or electrochemically. Chemical doping can be done by exposure of the (CH)<sub>x</sub> film to a known vapour pressure of a volatile dopant, e.g. I<sub>2</sub>, AsF<sub>5</sub>, etc., until the desired conductivity is obtained. Removal of the dopant vapour essentially 'freezes' the conductivity at that stage. Doping can also be done by treatment of the polymer film with a solution of the dopant in an appropriate solvent (e.g. I<sub>2</sub> in pentane, sodium naphthalide in THF) or by treatment with molten Na or K. Polyacetylene can act as an electron-source or as an electron-sink according to whether it is oxidized (doped *p*-type) or reduced (doped *n*-type). (CH)<sub>x</sub> begins to lose electrons at an applied potential of +3.10 volts and gains electrons at an applied potential of +1.75 volts versus a Li/Li<sup>+</sup> electrode. Electrochemical

doping can be carried out by using strips of  $(\text{CH})_x$  as anode and cathode. For example, when the electrodes, immersed in a solution of  $\text{LiClO}_4$  in propylene carbonate, are connected to a d.c. source (4V), oxidation of  $(\text{CH})_x$  occurs at the anode giving  $[(\text{CH})^+(\text{ClO}_4^-)]_x$  and reduction occurs at the cathode giving  $[\text{Li}^+(\text{CH})^-]_x$ . The possibility of reversible redox reactions of polyacetylene in an electrochemical cell forms the basis of light weight, high power-density, rechargeable storage batteries (Nigrey *et al.*, 1981).

A number of polyheterocycles have been prepared. For instance, oxidative electrochemical polymerization of pyrrole produces polypyrrole, invariably containing dopant anions from the electrolyte. A polypyrrole film containing  $\text{AsF}_6^-$  of about  $10\text{ }\mu\text{m}$  thickness, is produced when a mixture of 0.2 M pyrrole and 0.004 M tetra-*n*-butylammonium hexafluoroarsenate in dimethyl sulphate is electrolysed using indium-tin oxide anode and platinum cathode at a current density of  $2\text{ mA cm}^{-2}$  for 20 minutes. The polymer grows on the indium-tin oxide surface (Hotta *et al.*, 1983). The doped polymers so obtained can be converted into neutral polymers by immediate reversal of the polarity after electrochemical polymerisation. Polythiophene and poly(3-methylthiophene) are prepared by similar methods. Organometallic polymers possessing high electrical conductivity have also been prepared (Sheats *et al.*, 1984).

### 3.3 Microcrystalline particles and clusters (the finite solid state)

There is a distinct region of small aggregates or clusters which falls between the atomic (or molecular) domain and that of condensed matter. These small particles and clusters possess unique properties and have several technological applications. The formation of these particles involves a vapour-solid, a liquid-solid, a solid-solid or a vapour-liquid-solid type of phase change governed by nucleation and it is important that the size of the growing nucleus is controlled (Mutanli, 1981).

Microclusters of metals up to 500 atomic mass units (AMU) have been obtained by inert-gas vaporization-condensation; the metal vapour effuses from a hot cell through a narrow orifice. The mean particle size by this technique varies in the range 5–200 Å, the microclusters containing anywhere between 1 and 500 atoms (e.g.  $\text{Sb}_{1-500}$ ;  $\text{Bi}_{1-280}$ ). Mass spectroscopy has been used to determine sizes of such clusters. Granquist and Buhman (1976) have described an apparatus to synthesize particles in the range 30–60 Å diameter. The arc-plasma method has been employed to prepare microclusters of ceramic

materials such as tungsten carbide (50–80 Å) and silicon carbide (100–200 Å). Biphasic ceramic-metal composites of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  or  $\text{ZrO}_2$  with Cu, Pt, Sn or Ni have been prepared by a sol-gel process (Roy & Roy, 1984). The xerogel consists of a microcrystalline or a noncrystalline ceramic matrix in which the metallic component is dispersed as small islands.

Microcrystals made up of relatively larger particles (still in the submicron range) are useful in applications involving solid state diffusion (or reaction) and sintering. These are synthesized by any of the following techniques: spray-dry, freeze-dry, sol-gel, pyrogel (high-temperature spray) or liquid drying. Thus, the freeze-dry technique has been used to prepare  $\alpha$ - and  $\gamma$ - $\text{Fe}_2\text{O}_3$  (150–200 Å) while the sol-gel technique has been used to prepare  $\text{Y}_3\text{Fe}_5\text{O}_{12}$  and  $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$  (PZT). In all these techniques, one starts with aqueous solutions or mixed sols of the appropriate stoichiometry; the solutions are atomized and heat or mass transfer is achieved in milliseconds. The temperature of the sink (source) is around 300 K for sol-gelling (in a bath of 2-ethylhexanol and liquid drying in a bath of acetone), at 78 K for freeze-drying, around 600 K for spray-drying and around 1200 K for the pyrogel technique. The preparations enable homogeneity at molecular level, small grain size, low porosity, large surface area and theoretical density of sintered compacts.

Transmission and scanning electron microscopy are employed for a direct study of microclusters while the distribution of sizes (or average diameter) is provided by sedimentation and other techniques. The average particle diameter is obtained by the Brunauer-Emmett-Teller (BET) surface-area method and by X-ray line broadening.

Microcrystals exhibit properties distinctly different from those of bulk solids. The fractional change in lattice spacing has been found to increase with decreasing particle size in  $\text{Fe}_2\text{O}_3$ . Magnetic hyperfine fields in  $\alpha$ - $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  are lower in the microcrystalline phase compared to those of the bulk crystalline phases. The tetragonality (i.e. the departure of the axial ratio from unity) of ferroelectric  $\text{BaTiO}_3$  decreases with decrease in particle size; in PZT, the low-frequency dielectric constant decreases and the Curie temperature increases with decreasing particle size. The small particle size in microcrystals cannot apparently sustain low-frequency lattice vibrations.

### 3.4 Amorphous materials

It is only in recent years that there has been the realization that most materials can be rendered amorphous. Referring specifically to glasses, it may be said that most materials, if cooled fast enough (and far



enough) from the liquid state, can be made in the form of glasses. The various techniques available for the preparation of glasses (Angell, 1981, Elliott *et al.*, 1985) are cooling of supercooled liquid phases, vapour deposition, shock disordering, radiation disordering, desolvation and gelation (Fig. 3.5). All these techniques with the exception of the first produce materials which cannot easily be characterized, especially with regard to their entropies relative to those of the corresponding crystals.

A variety of glasses, possessing different types of bonding, have been prepared. In Table 3.5, we list a few of them along with their glass transition temperature to illustrate the universality of glass formation. The rate of cooling has to be very fast to prepare glasses from metallic materials; the temperature drop required is around 1000 degrees in a millisecond ( $\sim 10^6 \text{ K s}^{-1}$ ). Melt-spinning, where the metallic glass is spun off a copper rotor as a ribbon at a rate exceeding a kilometre per minute is employed for the purpose. Most other glasses prepared by quenching melts require slower rates;  $\text{SiO}_2$  requires a cooling rate of hardly  $0.1 \text{ K s}^{-1}$  and this is attained by allowing the melt to cool freely. *Splat-quenching* techniques with a range of cooling rates ( $10^5$ – $10^8 \text{ K s}^{-1}$ ) have also been employed to prepare metallic glasses. Of special interest is the technique of *laser-glazing* where the surface of a crystalline material is made glassy by exposing it to a moving focussed laser beam so that the subadjacent solid acts as heat sink; the quenching rate in this technique has been estimated at  $10^{11} \text{ K s}^{-1}$ .

The vapour deposition method is widely used to obtain amorphous solids. In this technique, atoms, molecules or ions of the substance (in

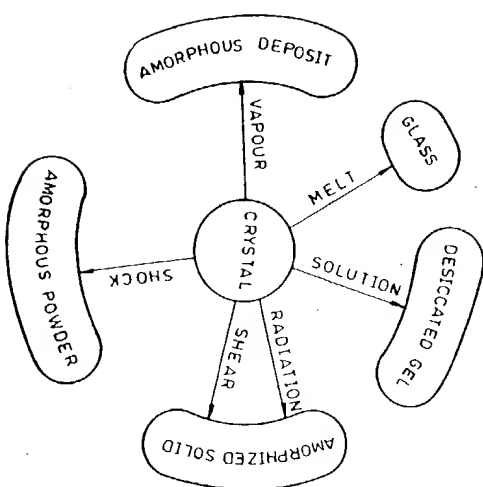


Figure 3.5. Various routes for preparing amorphous solids.

dilute vapour phase) are deposited on to a substrate maintained at a low temperature. Most vapour-deposited amorphous materials crystallize on heating, but some of them exhibit an intervening second-order transition (akin to the glass transition). Amorphous solid water and methanol show such transitions. The structural features of vapour-deposited amorphous solids are comparable to those of glasses of the same materials prepared by melt-quenching.

Disordering of crystalline materials by subjecting them to shock (e.g. as in the case of quartz and other minerals) or by large dosages of radiation (neutrons or alpha particles) also produces the amorphous state. The *metamict* form (Pabst, 1952) produced by irradiation is unstable with respect to the vitreous form. Substances such as magnesium acetate are rendered glassy by a desolvation process. In the gelation method, the material is first produced in gel form by hydrolysis of an organic derivative (e.g. ethyl silicate); the gel is then dried and collapsed into the glassy state.

Solid state reactions may also produce amorphous solids starting from crystalline solids. For instance, Yeh *et al.* (1983) have found that absorption of hydrogen by crystalline  $\text{Zr}_3\text{Rh}$  transforms it to a hydrided amorphous material.

### 3.5 Crystal growth

Crystals are essential both for fundamental studies of solids and for fabrication of devices. The ideal requirements are large size, high purity and maximum perfection (freedom from defects). It may also be

Table 3.5. Typical glassy amorphous solids

Substance	Nature of bonding	Glass transition, K
$\text{SiO}_2$	Covalent	1450
$\text{GeO}_2$	Covalent	820
$\text{As}_2\text{S}_3$	Covalent	470
Se	Covalent (Polymeric)	320
Polyvinylacetylene	Covalent (Polymer)	310
$\text{BeF}_2$	Ionic	570
75%AgI–25%Ag <sub>2</sub> SeO <sub>4</sub>	Ionic	75
$\text{Au}_{0.8}\text{Si}_{0.1}\text{Ge}_{0.1}$	Metallic	295
Propylene carbonate	van der Waals	160
Isopentane	van der Waals	65
$\text{H}_2\text{O}$	Hydrogen bonded	139(?)
$\text{C}_2\text{H}_5\text{OH}$	Hydrogen bonded	90
$\text{Fe}_{80}\text{B}_{20}$	Metallic	crystallizes

necessary to incorporate selective impurities (dopants) during growth in order to achieve required electronic properties. A number of methods is available for growing crystals (Table 3.6) and the subject has been reviewed extensively in the literature (Laudise, 1970; Banks & Wold, 1974; Mroczkowski, 1980; Honig & Rao, 1981).

The most common methods of growing crystals involve solidification from the melt (in the case of one-component systems) or crystallization from solution. Some of the methods for growing crystals from melt are described schematically in Fig. 3.6. In the *Czochralski method*, commonly known as the pulling technique, the material is melted by induction or resistance heating in a suitable nonreactive crucible. The melt temperature is adjusted to slightly above the melting point and a seed crystal is dipped into the melt. After thermal equilibration is attained, the seed is slowly lifted from the melt. As the seed is pulled, continuous growth occurs at the interface. The diameter of the growing crystal can be controlled by adjusting the rate of pulling, the rate of melt-

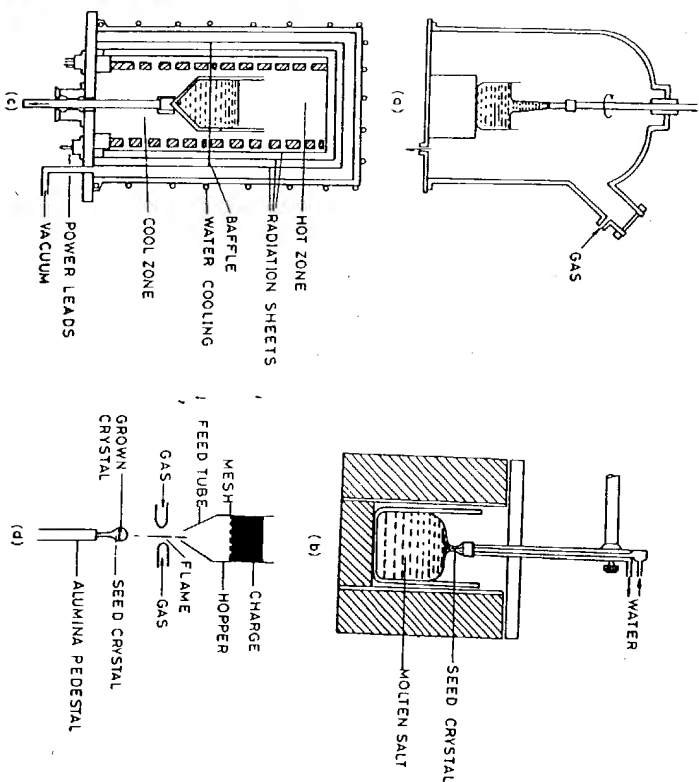
Table 3.6 Methods of Crystal growth

I. Growth in one-component systems	
(a) Solid-solid	Strain-annealing, devitrification or polymorphic phase change
(b) Liquid-solid	1. Directional solidification (Bridgman-Stockbarger)
	2. Cooled seed (Kyropoulos)
	3. Pulling (Czochralski and also triarc)
	4. Zoning (Horizontal zone, vertical zone)
	5. Flame fusion (Verneuil)
	6. Slow cooling in skull melter
(c) Gas-solid	Sublimation-condensation or sputtering
II. Growth involving more than one component	
(a) Solid-solid	Precipitation from solid solution
(b) Liquid-solid	1. Growth from solution (evaporation, slow cooling and temperature differential)
	(i) Aqueous solvent; (ii) Organic solvents; (iii) Molten solvents; (iv) Hydrothermal
	2. Growth by reaction
	(i) Chemical reaction; (ii) Electrochemical reaction
	3. Growth from melt; e.g. Congruently melting intermetallic compounds
(c) Gas-solid	1. Growth by reversible reaction (chemical vapour transport)
	2. Growth by irreversible reaction (epitaxial process).

level drop and the heat fluxes into and out of the system. The technique has the advantage that the growth interface does not come into contact with the walls of the crucible and hence formation of unwanted nuclei is avoided. The method has been used for the growth of silicon, germanium, III-V semiconductors, ceramic oxides like  $\text{Al}_2\text{O}_3$ , rare earth perovskites such as  $\text{LaAlO}_3$ ,  $\text{LaFeO}_3$ , garnets, scheelites, etc. Oxide materials can be grown in air while others require closed systems and atmosphere control. In the triarc method (described earlier in Section 3.2.4) the crystal is pulled from the melt. The *Kyropoulos method* is similar to the Czochralski method, but instead of pulling the seed crystal, the crystal-liquid interface moves into the melt as crystallization proceeds. In the *Bridgman-Stockbarger method*, a sharp temperature gradient is provided across the melt which results in nucleation in the colder region. The conical geometry of the crucible at the bottom limits the number of nuclei formed.

Another method for growing crystals from melt is the *floating zone*

Figure 3.6. Methods for crystal growth from melt: (a) Czochralski method; (b) Kyropoulos method; (c) Bridgman-Stockbarger method and (d) Verneuil method.



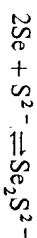
technique in which a section of the starting material, held vertically in the form of a rod, is melted by suitable heating. As the molten zone is moved along the rod, progressive melting of the sample at one end of the zone and crystal growth at the other end occur. If a seed crystal is provided at one end, the whole rod can be converted into a single crystal. The method has the advantage that there is no contamination from the crucible. The method is similar to purification by *zone-refining* and has been used routinely to grow single crystals of silicon. In the *flame fusion* (*Vernuij*) method, the powder sample is directly fed into an oxy-hydrogen flame and the melt allowed to drip on a seed crystal. As crystallization occurs on the top, the growing seed is lowered slowly, facilitating the growth of large crystals. The method has been used for the growth of high-melting oxides such as ruby and sapphire. A variant of the flame fusion technique is the *plasma torch method* in which the powder is dropped through a hot plasma generated and maintained by high-frequency current. The skull technique (see Section 3.2.5) has emerged to become a useful method for growing large crystals of several oxides.

Frequently, growth of crystals from melt involves more than one component, such as impurities, intentionally added dopants, etc., in addition to the major component. In these cases, it is essential to know the distribution of the second component between the growing crystal and the melt. This distribution occurs according to the phase diagram relating the equilibrium solubilities of the second component (impurity) in the liquid and the solid phases.

A number of crystal-growth methods making use of the solubility of a solute in a suitable solvent are known. Crystallization requires supersaturation, which can be provided by a temperature difference between the dissolution and growth zones, by solvent-evaporation or by a chemical reaction. In the solution methods, it is difficult to avoid contamination of the product by other components in the solution or flux. The flux technique has nevertheless been used to grow crystals of  $\text{GeO}_2$ ,  $\text{SiO}_2$ ,  $\text{BaTiO}_3$ ,  $\alpha\text{-Al}_2\text{O}_3$ ,  $\text{GdAlO}_3$  and so on. The role of the solvent is to depress the melting point of the solute to be grown as a crystal. Although supersaturation is required for crystal growth, experimentally it is found that growth rate from solution is enormously faster than expected, considerable growth occurring even at low degrees of supersaturation (1%). This discrepancy was explained by Frank and Cabrera in terms of the effect of dislocations on crystal growth. Whereas the growth of a perfect crystal requires nucleation of a new layer on a perfect surface after completion of the previous layer, in the presence of a screw dislocation, growth does not require nucleation of a new layer. The dislocation provides a stepped surface where growth can occur even at

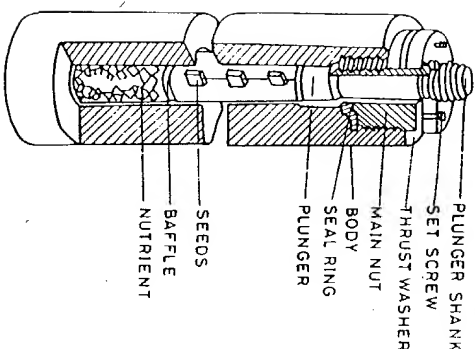
low degrees of supersaturation. Spiral growth patterns arising from screw dislocations have been observed on a number of crystals grown from solution and vapour supporting the Frank model.

Among the solution-growth methods, crystallization from aqueous solution is well known. Materials with low water solubility may be brought into solution by the use of complexing agents (mineralizers). Selenium, for instance, can be grown from aqueous sulphide solutions, by making use of the reaction



An important method for growth of crystals with low water solubility is the hydrothermal method discussed earlier in Section 3.2.3. Hydrothermal synthesis is generally carried out with an autoclave of the type shown in Fig. 3.7. The autoclave consists of a lower nutrient region and an upper growth region separated by a baffle. The solute is placed in the nutrient region and a few seed crystals are suspended in the growth region. The vessel is filled with water to a predetermined volume, mineralizers are added if necessary, then it is closed and the temperature raised while providing a gradient. Since the solubility of most substances increases with increasing temperature, the nutrient region is maintained at a higher temperature than the growth region. The solvent saturates at the dissolving zone, moves by convection to the cooler growth zone where it is supersaturated and deposits the solute on the seed crystal. The solution is undersaturated when it reaches the nutrient region, thus dissolving more solute and the cycle goes on. Large quartz

Figure 3.7. Apparatus for hydrothermal synthesis.





crystals are grown by this method. If the solute happens to have a retrograde solubility, as in the case of  $\text{AlPO}_4$ , the temperature gradient has to be reversed between the growth and the nutrient regions. In hydrothermal synthesis, the degree of filling the autoclave with solvent is an important factor; it has to be more than 32% in order to provide a high density of the solvent. Conventionally, hydrothermal experiments are carried out in alkaline medium, the  $\text{OH}^-$  ion acting as complexing agent. Hydrothermal synthesis has been used to stabilize unusual oxidation states in transition metal compounds and to synthesize low-temperature and metastable phases (Rabenu, 1985).

Insoluble ionic solids such as  $\text{CaCO}_3$  and  $\text{BaSO}_4$  cannot be grown by conventional solution methods or even by controlled chemical reaction because of instantaneous precipitation of the product when the reactants are mixed. The *gel method* is useful for the growth of such solids; this simple method depends on controlled diffusion of the reagents through the gel. A U-tube is filled with silica gel produced by acidifying a solution of sodium metasilicate (Fig. 3.8). The reagents are added to the two arms of the U tube; they diffuse slowly towards one another. In local regions where the concentration exceeds the solubility product, nuclei are formed and grow further into large crystals. Hensch and coworkers (1965) have made use of this method to grow crystals of calcium tartrate, calcium tungstate and lead iodide and have even incorporated selective impurity ions ( $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$  etc.) during growth.

Solids such as  $\text{KF}$ ,  $\text{PbO}$ ,  $\text{PbF}_2$  and  $\text{B}_2\text{O}_3$  are powerful solvents (flux) in the molten state for many inorganic substances and hence can be used as media for the growth of crystals. The usual technique is to dissolve the solute in a suitable combination of flux contained in a platinum crucible while maintaining the temperature slightly above the saturation point. After the crucible has been cooled at a programmed rate, the flux is poured off or leached away by mineral acid, leaving behind the crystals.

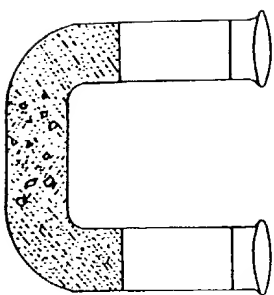


Figure 3.8. Gel method for growth of water-insoluble ionic solids.

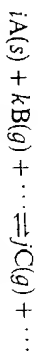
Yttrium iron garnet and its isomorphs are typical examples of solids grown by the *flux method* using  $\text{PbO}$ – $\text{PbF}_2$  fluxes. A recent development relating to growth of crystals from molten media is the use of molten metals as solvents from which crystals of intermetallic compounds are grown. Crystals of rare earth borides,  $\text{LnB}_4$  and  $\text{LnB}_6$ , have been grown from liquid aluminium and rare earth rhodium stannides from molten tin (Fisk *et al.*, 1972; Espinosa, 1980).

Electrolysis of molten salt solutions has been applied for preparation and crystal growth (Banks & Wold, 1974; Wold & Bellavance, 1972; Feigelson, 1980). The *electrolytic method* involves reduction, usually, of a cation and deposition of a product containing the reduced cation at the cathode. The technique was used by Andrieux and coworkers for the synthesis of a variety of transition metal compounds. Typical examples are: (i) growth of vanadium spinels,  $\text{MV}_2\text{O}_4$  ( $\text{M} = \text{Mn, Fe, Co, Zn}$  and  $\text{Mg}$ ), from  $\text{Na}_2\text{B}_4\text{O}_7$  and  $\text{NaF}$  melts using carbon crucibles and a carbon cathode (iron crucible and iron cathode for the iron compound), (ii) synthesis of  $\text{NaMo}_2$  ( $\text{M} = \text{Fe, Co, Ni}$ ) by the electrolysis of  $\text{NaOH}$  melts contained in alumina crucibles and  $\text{M}$  electrodes, (iii) synthesis of alkali metal tungsten bronzes,  $\text{A}_x\text{WO}_3$ , by the electrolysis of alkali metal tungstates using platinum electrodes. Although most of the early studies of fused-salt electrolysis were empirical, aimed at obtaining large single crystals by manipulating melt composition and current density, later studies as exemplified by the work of Whittingham and Huggins (1972) on the preparation of alkali metal tungsten bronze, have shown that if the potential difference across the cell rather than the current density is kept constant during electrolysis, crystals of fixed composition can be grown. The electrolysis method has been employed for the preparation and growth of crystals of a wide variety of solids such as borides, carbides, silicides, phosphides, arsenides, and sulphides.

The experimental cell assembly for electrolytic growth can be exceedingly simple or complex, depending on the system studied. For example, electrolytic growth of alkali metal tungsten bronzes requires a Gooch crucible set inside a bigger Gooch crucible, the inner crucible serving as the anode chamber and the outer one as the cathode chamber; electrodes of platinum or gold are used. No inert atmosphere is necessary since atmospheric oxygen has no influence upon the current–potential relationship. In contrast to this, the electrolytic cell used by Didenko and Litz (1962) for the synthesis of  $\text{CeS}$  and  $\text{ThS}$  is quite elaborate, consisting of graphite and aluminium crucibles (serving as electrode compartments) together with molybdenum electrodes and involving a provision for inert atmosphere.

Growth of crystals from vapour may be divided into two categories

depending on whether the change, vapour  $\longrightarrow$  crystal, is physical or chemical. When the composition of the vapour and the crystal is the same, the process is physical; examples are sublimation-condensation and sputtering. The process is termed chemical when a chemical reaction occurs during the growth; in such a case, the composition of the solid is different from the vapour. The use of chemical vapour deposition (CVD) as a preparative technique was discussed earlier in this chapter (see Section 3.2.6). We shall now briefly discuss the related *chemical vapour transport* (CVT) which is useful both for preparation of new solids as well as growing them into crystals. The method has been treated extensively by Schäfer (1972) and Rosenberger (1981). In CVT, a condensed phase reacts with a gas to form volatile products. An equilibrium exists between the reactants and products:



CVT makes use of the temperature dependence of the above heterogeneous equilibrium to transport solid A through the vapour phase by means of gaseous intermediate(s) C. That the process involves true transport and not just evaporation and condensation is evident from the fact that solid A does not possess an appreciable vapour pressure at the experimental temperature; moreover, transport of A is not observed without the transporting agent B.

Chemical transport is normally carried out by maintaining a temperature difference between the charge end and growth end in a closed system (Fig. 3.9). The forward reaction occurs at the charge-end forming gaseous products and the reverse reaction occurs at the growth-end depositing crystals. The temperatures  $T_1$  and  $T_2$  chosen at the growth-end and charge-end respectively depend on whether the reaction is endothermic or exothermic. For endothermic reactions, transport requires that  $T_2 > T_1$ ; the reverse is true for exothermic reactions. The factors that determine growth of crystals by this method are, the choice of the chemical reaction chosen for transport (the CVT equilibrium should not lie at extremes lest the reversal becomes difficult), and the magnitude of  $T_1$  and  $T_2$  chosen and the concentration of transport agent used. The examples listed in Table 3.7 clearly suggest

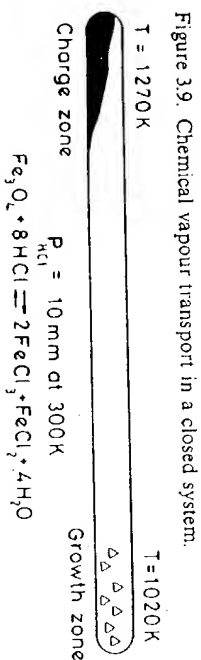


Figure 3.9. Chemical vapour transport in a closed system.

that the method can be used to prepare or grow crystals of almost any type of solid material provided a suitable transporting agent that can give volatile products can be found. Metals have been transported using the volatile halides.

CVT is indeed a popular technique and has been employed to grow crystals of oxide phases such as  $V_8O_{13}$ , free from contamination by the neighbouring Magnéli phases,  $V_7O_{13}$  and  $V_9O_{17}$ . The transporting agents commonly used are  $I_2$ ,  $TeCl_4$  and  $Cl_2$ . When a metal oxide can be

volatilized readily (e.g.  $SnO_2 \xrightarrow{\text{heat}} SnO + \frac{1}{2}O_2$ ), the vapour species formed can be recombined to form single crystals at the cooler end.

*Molecular beam epitaxy* is an important technique for the preparation of semiconductors (III-V compounds). The finesse and sophistication of modern preparative solid state science is exemplified by this method which employs reactions of multiple molecular beams with a single crystal substrate.

When a polycrystalline solid sample is heated for a sufficient length of time below its melting point, an increase in the average size of crystals is observed. The driving force for this change is the lowering of outer crystalline area. The number of crystals obtained depends on the number of active nuclei capable of growing at the expense of the polycrystalline matrix. Metals are normally grown as crystals in the solid state by the so-called 'strain-anneal' procedure involving recrystallization by annealing out strain. Growth in the solid state is particularly useful for solids exhibiting incongruent melting or showing a polymorphic transition below the melting point.

Table 3.7 Some crystals grown by chemical vapour transport method

Starting material	Final product (crystals)	Transport agent	Temperature, K
$SiO_2$	$SiO_2$	HF	470 $\longrightarrow$ 770
$Fe_3O_4$	$Fe_3O_4$	HCl	1270 $\longrightarrow$ 1070
$Cr_2O_3$	$Cr_2O_3$	$Cl_2 + O_2$	1070 $\longrightarrow$ 870
$MO + Fe_2O_3$ (M = Mg, Co, Ni)	$MFe_2O_4$	HCl	—
$Nb + Nb_2O_5$	NbO	$Cl_2$	—
$NbSe_2$	$NbSe_2$	$I_2$	1100 $\longrightarrow$ 1050

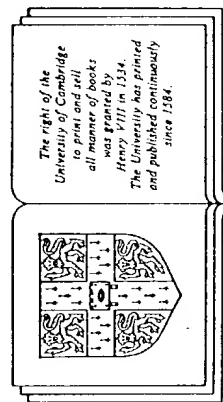
**ATTACHMENT B**

C. N. R. RAO, FRS  
J. GOPALAKRISHNAN

*Solid State and Structural Chemistry Unit, Indian Institute of Science,  
Bangalore, India*

# **New directions in solid state chemistry**

Structure, synthesis, properties, reactivity  
and materials design



**CAMBRIDGE UNIVERSITY PRESS**

*Cambridge*

*London New York New Rochelle*

*Melbourne Sydney*

SCICOL  
QD  
478  
R36  
1986

## Contents

Preface	ix
1 Structure of solids: old and new facets	1
1.1 Introduction	1
1.2 Description of crystals	2
1.3 Bonding in crystals	4
1.4 Inorganic structures	13
1.5 Silicates and aluminosilicates	34
1.6 Nonbonded interactions in ionic crystals	39
1.7 New ways of looking at the structures of inorganic solids	42
1.8 Polytypism	50
1.9 Organic crystal structures	53
1.10 Inclusion compounds and clathrates	56
1.11 Noncrystalline or amorphous solids	60
1.12 Quasicrystals	65
1.13 Models and graphics	65
1.14 Solitons	66
2 New and improved methods of characterization	67
2.1 Introduction	67
2.2 Structural characterization	68
2.2.1 X-ray diffraction	70
2.2.2 Electron diffraction	71
2.2.3 Neutron diffraction and related techniques	73
2.2.4 Electron microscopy	75
2.2.5 X-ray absorption spectroscopy (EXAFS and XANES)	84
2.2.6 Nuclear magnetic resonance spectroscopy (MASNMR)	95
2.2.7 Electron spectroscopies	99
2.2.8 Other spectroscopic techniques	105
2.2.9 Concluding remarks	106
2.3 Characterization of composition and purity	107
3 Preparative strategies	112
3.1 Introduction	112
3.2 Preparation of crystalline materials	116
3.2.1 Ceramic methods	116

Published by the Press Syndicate of the University of Cambridge  
The Pitt Building, Trumpington Street, Cambridge GB2 1XP  
32 East 57th Street, New York, NY 10022, USA  
10 Stanford Road, Oakleigh, Melbourne 3166, Australia

© Cambridge University Press 1986

First published 1986

Printed in Great Britain at the University Press, Cambridge

*British Library cataloguing in publication data*

Rao, C. N. R.

New directions in solid state chemistry: structure, synthesis, properties reactivity and materials design. — (Cambridge solid state science series)

1. Solid state chemistry

I. Title II. Gopalakrishnan, J.

541'.0421 QD478

*Library of Congress cataloguing in publication data*

Rao, C. N. R. (Chintamani Nagesa Ramachandra), 1934—  
New directions in solid state chemistry.

(Cambridge solid state science series)

Includes bibliographical references.

1. Solid state chemistry. I. Gopalakrishnan,

J. (Jagannatha), 1939— II. Title. III. Series.

QD478.R36 1986 541'.0421 85-22329

ISBN 0 521 301920

TM

5.5.4. Fluorite-related solids	237
5.6. Crystallographic shear	240
5.7. Block structures	244
5.8. Infinitely adaptive structures	247
5.9. Intergrowths	248
5.10. Defect perovskite oxides: a case study	252
<b>6. Structure-property relations</b>	<b>264</b>
6.1. Introduction	264
6.2. Electrons in solids	264
6.2.1. Band model	265
6.2.2. Localized electron model	268
6.2.3. Chemical bond approach	269
6.3. Properties	272
6.3.1. Magnetic properties	273
6.3.2. Electrical properties	284
6.3.3. Superconductivity	289
6.3.4. Dielectric and optical properties	292
6.4. Case studies	297
6.4.1. Metal oxides	297
6.4.2. Metal sulphides	311
6.4.3. Metal fluorides	320
6.5. Metal-nonmetal transitions	327
6.6. Metal clusters	339
6.7. Mixed-valence compounds	342
6.8. Low-dimensional solids	351
6.9. Ferroics	359
6.10. Liquid crystals	372

## 7 Fashioning solids for specific purposes: aspects of materials design

7.1. Introduction	377
7.2. Fast ion conductors	377
7.3. Photoelectrochemistry	378
7.4. Magnetic materials	386
7.5. Hydrogen storage materials	394
7.6. Amorphous materials	399
7.7. Organic materials	405
7.8. Langmuir-Blodgett films	409
7.9. Liquid crystals	413
7.10. Nonlinear optical materials	413
7.11. Luminescent inorganic materials	416

3.2.2. Chemical methods	118
3.2.3. High pressure methods	124
3.2.4. Arc techniques	130
3.2.5. Skull melting	132
3.2.6. Chemical vapour deposition (CVD)	132
3.2.7. Synthesis of organic solids	133
3.3. Microcrystalline particles and clusters (the finite solid state)	136
3.4. Amorphous materials	137
3.5. Crystal growth	139
<b>4 Phase transitions</b>	<b>148</b>
4.1. Introduction	148
4.2. Thermodynamics	148
4.3. Soft modes	153
4.4. Central peaks	156
4.5. Critical phenomena	157
4.6. Structural changes in phase transitions	158
4.7. Mechanisms of phase transitions	161
4.8. Organic solids	164
4.9. Incommensurate phases	166
4.10. Cooperative Jahn-Teller effect	176
4.11. Spin-state transitions	181
4.12. The plastic crystalline state	190
4.13. The liquid crystalline state	195
4.14. Noncrystalline state and the glass transition	200
4.15. Monte Carlo and molecular dynamics methods	204
4.16. Applications of phase transitions	206

## 5 New light on an old problem: defects and nonstoichiometry

5.1. Introduction	208
5.2. Point defects	208
5.2.1. Point defect equilibria	211
5.2.2. Paraelectric and molecular impurities in ionic solids	214
5.2.3. Colour centres	220
5.3. Dislocations	222
5.4. Planar defects	223
5.5. Ordered point defects and superstructures	227
5.5.1. Doped alkali halides	230
5.5.2. Metal chalcogenides and carbides	230
5.5.3. Metal oxides of rock salt structure	231

7.12	Laser materials	419
<b>8</b>	<b>Reactivity of solids</b>	<b>421</b>
8.1	Introduction	421
8.2	Nature of solid state reactions	421
8.3	Reactions involving a single solid phase	422
8.4	Solid-gas reactions	426
8.5	Solid-solid reactions	430
8.6	Solid-liquid reactions	434
8.7	Intercalation chemistry	434
8.8	Reactions of organic solids	449
8.9	Heterogeneous catalysis	460
	<b>References</b>	<b>475</b>
	<b>Index</b>	<b>505</b>

## Preface

Although solid state science is an area of intense research activity pursued by physicists and materials scientists, the contributions of chemists to this area have a distinct identity. The great skill of chemists in developing novel methods for the synthesis of complex materials, and their understanding of the intricacies of structure and bonding, make their contributions to solid state science unique. At the present time, solid state chemistry is mainly concerned with the development of new methods of synthesis, new ways of identifying and characterizing materials and of describing their structure and above all, with new strategies for tailor-making materials with desired and controllable properties be they electronic, magnetic, dielectric, optical, adsorptive or catalytic. It is heartening that solid state chemistry is increasingly coming to be recognized as an emerging area of chemical science.

In this monograph, we have attempted to present the highlights of modern solid state chemistry and indicate the new directions in a concise manner. In doing so, we have not described the varied principles, properties and techniques that embody this subject at length, but have concerned ourselves with the more important task of bringing out the flavour of the subject to show how it works. We believe that the material covered is up to date, taking the reader to the very frontiers of the subject. We have been careful to include some introductory material for each aspect in order to enable students and beginners to benefit from the book. Instead of dividing the book into the traditional chapters (dealing with crystal chemistry, properties of solids, reactivity and so on) we have tried to present the subject in a style that would reflect the way the subject is growing today. Because of this approach, the lengths of the different chapters have inevitably become somewhat variable.

We hope that the book will be found useful by practitioners of solid state science, especially chemists interested in the study of condensed matter. While the book can certainly be used as a supplementary text in a broad course on solid state science, it could form the basis of a well-planned course in solid state chemistry. We shall be more than rewarded if the book is found useful by students, teachers and practitioners of solid state chemistry.

We have cited important material from the very recent literature including some of the latest references, but in dealing with some of the

### 3 Preparative strategies

#### 3.1 Introduction

Availability of pure, well-characterized solid samples is crucial to all solid state studies. A knowledge of the various experimental methods available for the preparation of solids therefore becomes an important and integral part of solid state chemistry (Hagenmuller, 1972; Honig & Rao, 1981). A brief reflection on the development of solid state science reveals that, in many cases, it is the synthesis of a novel compound that has triggered off a new line of research. Tables 3.1 and 3.2 provide a few examples to illustrate the point. To many solid state

Table 3.1 *Some early solid state preparations that have led to major developments.*<sup>a</sup>

Prototype	First reported by (year)	Subsequent development
InP	Thiel (1910)	III-V semiconductors
ZrO <sub>2</sub> (CaO)	Ruff (1929)	Solid electrolyte, oxygen sensor
Na $\beta$ -alumina	Stillwell (1926)	Solid electrolyte, Na-S battery
V <sub>3</sub> Si	Wallbaum (1939)	Al5 high temperature superconductors
BaTiO <sub>3</sub>	Tammann (1925)	Ferroelectrics, ceramic capacitors
LiNbO <sub>3</sub>	Süe (1937)	Nonlinear optics
BaFe <sub>12</sub> O <sub>19</sub>	Adelsköld	Ferrites, memory devices
LnNi <sub>5</sub> (Ln = rare earth)	Schrevelius (1938) Klemm (1943)	Strong magnets, hydrogen storage materials
Amorphous Si	König (1944)	Solar cells
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>3</sub> X:Sb <sup>3+</sup> , Mn <sup>2+</sup>	McKeag, Ranby	Fluorescent lamp phosphor
ZnS/CdS	Jenkins (1949) Kröger (1940)	Cathode ray tube phosphor

<sup>a</sup>Partly taken from the US Panel Report on New Materials published by Centre for Materials Research, Stanford University (1979).

scientists, preparation of solids may mean preparation of single crystals of elements or simple compounds (e.g. Si, Ge, III-V semiconductors, alkali halides, etc.) for a study of a specific property or for technical applications. Preparation of solids is, however, a much more general activity, particularly amenable to chemists. A variety of strategies are adopted to prepare solids and to grow crystals. Technological advances have enabled solid state chemists to employ a broad range of conditions for preparative purposes. Ultra-rapid quenching of materials from very high temperatures, irradiation heating by intense laser beams, melting of solids by electron-beam heating or by the skull method and use of high pressures have become common procedures. When noncrystalline solids are required, they are prepared by sputtering, quenching and a number of other methods. To meet the challenge of producing materials which have hitherto required high temperatures, advantage is often taken of simple chemical methods.

Four categories of preparation of solids can be distinguished: (i) preparation of a series of compounds in order to investigate a specific property, as exemplified by a series of perovskite oxides to examine their electrical properties or by a series of spinel ferrites to screen their magnetic properties; (ii) preparation of unknown members of a structurally related class of solids to extend (or extrapolate) structure-property relations, as exemplified by the synthesis of layered chalcogenides and their intercalates or new derivatives of TTF-TCNQ to study their superconductivity; (iii) synthesis of a new class of compounds (e.g. sialons, (Si, Al)<sub>3</sub>(O, N)<sub>4</sub>, or doped polyacetylenes) and (iv)

Table 3.2. *Some recently synthesized materials of technological relevance.*

Sialon (Si, Al) <sub>3</sub> (O, N) <sub>4</sub>	High temperature ceramics
Sm <sub>0.4</sub> Y <sub>2.6</sub> Ga <sub>1.2</sub> Fe <sub>3.8</sub> O <sub>12</sub>	Bubble memory devices
M <sub>4</sub> Mo <sub>6</sub> Se <sub>8</sub> and related Chevrel phases	High field superconductors
LnRh <sub>4</sub> B <sub>4</sub> (Ln = rare earth)	Coexistence of superconductivity and magnetism
Aluminosilicates (including ZSM-5)	Catalysis (e.g. methanol-gasoline)
Pb <sub>2</sub> Ru <sub>2-x</sub> Pb <sub>x</sub> <sup>2+</sup> O <sub>7-y</sub>	Electrocatalyst (for use in oxygen electrodes)
Polyacetylene (n- and p-type doping)	Solid state batteries
Diacytlenes polymers	Nonlinear optic materials (better than LiIO <sub>3</sub> )
Organic liquid crystals	Display devices



preparation of known solids of prescribed specifications (crystallinity, shape, purity, etc.) as in the case of crystals of Si, III-V compounds and alkali halides. Category (iii) is a challenge that chemists respond to.

An understanding of the crystal chemistry is of the essence in designing new materials possessing desired properties. It is only when we have the correct prescription of structure (in relation to the properties of interest) that we can start synthetic efforts. As discussed in Chapter 1, even in metal oxides alone, we have several structures such as perovskites, spinels, bronzes and pyrochlores; new families have been identified during characterization and structural elucidation of oxides. Accordingly, several of the homologous series of oxides (see Table 3.3) have been identified through X-ray crystallography or electron microscopy rather than by chemical analysis, the precise compositions often being identified by structural considerations. Preparative solid state chemistry becomes most rewarding when there is close interaction between preparation, characterization (including structure determination) and study of properties. In what follows, we shall discuss the methods of preparation of solids in various states of aggregation ranging from the amorphous and the microcrystalline states to polycrystalline powders and finally to single crystals.

It is helpful to make a distinction between the preparation of new Table 3.3 Some homologous series of metal oxides.

$\text{Ti}_n\text{O}_{2n-1}$	$4 \leq n \leq 9$ or $16 < n < 36$
$\text{Mo}_n\text{O}_{3n-1}$	$8 \leq n \leq 12$
$\text{W}_n\text{O}_{3n-2}$	$n = 20, 24, 25$ , etc.
$\text{Pr}_n\text{O}_{2n-2}$	$n = 4, 7, 9, 10, 11$ and $12$
$\text{Bi}(\text{WO}_3)_n$	$n = 6, 8, 15$ , etc.
$\text{Bi}_2\text{W}_n\text{O}_{3n+3}$	$n = 1, 2$ and $3$
$\text{La}_n\text{Ni}_n\text{O}_{3n-1}$	$n = 2$ and above
$\text{La}_n\text{Co}_n\text{O}_{3n-1}$	$n = 2$ and above
$(\text{Bi}_2\text{O}_3)[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$	$\text{A} = \text{Ba, Bi, etc.}$ $\text{B} = \text{Ti, Nb, W, Fe, Cr}$ $n = 1-8$
$\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$	$\text{A} = \text{Sr; B} = \text{Ti}$ $\text{A} = \text{La; B} = \text{Ni}$ $n = 1, 2, 3$ , etc.
$\text{A}_n\text{B}_n\text{O}_{3n+2}$	$\text{A} = \text{Na, Ca}$ $\text{B} = \text{Nb}$ $n^* = 4, 5, 6$ and $7$

\*Between  $n = 4$  and  $4.5$ , a large number of coherent intergrowth phases with long periodicities are known in this system (Portier *et al.*, 1975).

solids and the preparation of solids by new methods. Preparation of a new solid need not necessarily involve a new method. A number of instances can be cited where preparation of new solids with novel structures and properties is achieved by routine procedures. Typical of them are  $\text{Na}_3\text{Zr}_2\text{PSi}_2\text{O}_{12}$  (NASICON),  $\text{Na}_{1+x}\text{Al}_{11}\text{O}_{17+x/2}$  ( $\beta$ -alumina),  $\text{BaFe}_{12}\text{O}_{19}$  and  $\text{MMo}_6\text{S}_8$  ( $\text{M} = \text{Cu, Pb}$  etc.) Chevrel phases. All these solids are prepared by the ordinary method of reacting readily available constituents at elevated temperatures (the *ceramic method*). In the last case, the reaction is carried out in closed ampoules for the obvious reasons, but in others even this precaution is unnecessary. The importance of such preparations lies not in the method, but in selecting the right constituents in the right proportion, bearing in mind the chemistry as well as the structure and properties desired in the new phase. This aspect is illustrated by the synthesis of  $\text{Na}_3\text{Zr}_2\text{PSi}_2\text{O}_{12}$ , a fast sodium ion conductor, where the composition was chosen keeping in mind the coordination preferences of the atoms involved, the stability of their oxidation states, the nature of the network that would be formed and whether the network would permit three-dimensional mobility of sodium ions (Goodenough *et al.*, 1976). Another example of innovative synthesis by design is the preparation of synthetic bone material for prosthetic application (Roy, 1977). Here the problem is not only the synthesis of the chemical compound constituting the human bone, viz. calcium hydroxyapatite, but also having it with the 100% connectivity and porosity of the natural bone. The synthesis could be accomplished because of two realizations: certain marine corals ( $\text{CaCO}_3$ ) possess the same porosity and connectivity as the human bone and the aragonite form of  $\text{CaCO}_3$  can be topotactically converted to calcium hydroxyapatite in a hydrothermal reaction. Thus, the reaction of marine corals with phosphoric acid under hydrothermal conditions produces synthetic bone material.

Synthesis of new solids is not always achieved by design. Preparative solid state chemistry has its share of serendipitous discovery of new materials. The discovery of  $\text{NaMo}_4\text{O}_6$ , the prototype of metal cluster chain compounds, is an example of this category (Torardi & McCauley, 1979). The discovery resulted from a most innocent experiment aimed at preparing  $\text{NaZn}_2\text{Mo}_3\text{O}_8$ , the sodium-analogue of the lithium-containing cluster compound,  $\text{LiZn}_2\text{Mo}_3\text{O}_8$ . For this purpose, a mixture of  $\text{Na}_2\text{MoO}_4$ ,  $\text{ZnO}$ ,  $\text{MoO}_3$  and  $\text{Mo}$  was sealed in a molybdenum tube and heated at 1370 K. The product turned out to be shiny needles of  $\text{NaMo}_4\text{O}_6$  instead of the expected  $\text{NaZn}_2\text{Mo}_3\text{O}_8$ . The crystal structure of  $\text{NaMo}_4\text{O}_6$  turned out to be one of the most unique

oxide structures, consisting of infinite chains of  $\text{Mo}_6$  octahedral clusters sharing opposite edges (Fig. 1.17).

### 3.2 Preparation of crystalline materials

#### 3.2.1 Ceramic methods

The most common method of preparing solids is by the reaction of the component materials at elevated temperatures. If all the components are solids, the method is called the *ceramic method*. If one of the constituents is volatile or sensitive to the atmosphere, the reaction is carried out in sealed evacuated capsules. Ternary oxides, sulphides, phosphides, etc. have been prepared by this method. A knowledge of the phase diagram is generally helpful in fixing the desired composition and conditions for synthesis. Some caution is necessary in deciding the choice of the container; platinum, silica and alumina containers are generally used for the synthesis of metal oxides, while graphite containers are suitable for sulphides and other chalcogenides as well as pnictides.

Ceramic preparations often require relatively high temperatures (up to 2300 K) which can generally be attained by resistance heating. Electric arc and skull techniques can give temperatures up to 3300 K while high power  $\text{CO}_2$  lasers can give temperatures up to 4300 K.

Ceramic methods suffer from several disadvantages: (i) When no melt is formed during the reaction, the entire reaction has to occur in the solid state, first by a phase boundary reaction at the points of contact between the components and later by diffusion of the constituents through the product phase. With the progress of the reaction, diffusion paths become longer and longer and the reaction rate slower and slower; the reaction can be speeded up to some extent by intermittent grinding between heating cycles. (ii) There is no way of monitoring the progress of the reaction in a ceramic method. It is only by trial and error that one decides appropriate conditions that lead to the completion of the reaction. Because of this difficulty, one often ends up with mixtures of reactants and products by the ceramic technique. Separation of the desired product from such mixtures is difficult, if not impossible. (iii) Frequently, it becomes difficult to obtain a compositionally homogeneous product by a ceramic technique even where the reaction proceeds almost to completion.

Despite these limitations, ceramic techniques have been widely used for solid state synthesis. Mention must be made, among others, of the successful use of this technique for the synthesis of rare earth mono-

chalcogenides such as  $\text{SmS}$  and  $\text{SmSe}$ . The method (Jayaraman *et al.*, 1975) consists of heating the elements, first at lower temperatures (870–1170 K) in evacuated silica tubes; the contents are then homogenised, sealed in tantalum tubes and heated at  $\sim 2300$  K by passing a high current through the tube. Metal-rich halides of lanthanides and other early transition elements have been synthesized using tantalum containers (Corbett, 1980, 1981). Several halides and chalcogenides possessing condensed metal clusters have also been prepared by the ceramic method (Simon, 1981). Metal-rich suboxides of alkali metals have been prepared by reacting the metal with required amounts of oxygen until the gas is entirely absorbed ( $p < 10^{-5}$  torr) (Simon, 1975). Examples of such phases are  $\text{Rb}_6\text{O}$ ,  $\text{Rb}_9\text{O}_2$ ,  $\text{Cs}_{11}\text{O}_3$ ,  $\text{Cs}_3\text{O}$ ,  $\text{Cs}_4\text{O}$  and  $\text{Cs}_7\text{O}$ . Extreme air sensitivity and low temperatures of decomposition/melting render the preparation and investigation of the phases very difficult. These oxides are therefore investigated *in situ*.

Various modifications of the ceramic technique have been employed to overcome some of the limitations. One of these relates to decreasing the diffusion path lengths. In a polycrystalline mixture of reactants, the individual particles are of approximately  $10\text{ }\mu\text{m}$  size, which represents diffusion distances of roughly 10 000 unit cells. By using freeze-drying, spray-drying, coprecipitation and sol-gel and similar techniques, it is possible to bring down the particle size to a few hundred angstroms (see Section 3.3) and thus effect a more intimate mixing of the reactants. In *spray-drying*, suitable constituents dissolved in a solvent are sprayed in the form of fine droplets into a hot chamber. The solvent evaporates instantaneously leaving behind an intimate mixture of reactants, which on heating at elevated temperatures gives the product. In *freeze-drying*, the reactants in a common solvent are frozen by immersing in liquid nitrogen and the solvent removed at low pressures. In *coprecipitation*, the required metal cations are coprecipitated from a common medium, usually as hydroxides, carbonates, oxalates, formates or citrates, which are subsequently heated at appropriate temperatures to yield the final product. These methods have been used for the preparation of polycrystalline samples of several oxides such as ferrites, perovskites and  $\beta$ -alumina. The *sol-gel process* (Johnson, 1981) involves forming a concentrated sol of the reactant oxides or hydroxides and converting it to a semirigid gel by removing the solvent. The solvent is removed by passing fine droplets of the sol through a column of an aliphatic alcohol (e.g. 2-ethyl-1-hexanol). The dehydrated gel is heated at an appropriate temperature to obtain the product. Several complex oxide materials such as NASICON,  $\text{PbTi}_{1-x}\text{Zr}_x\text{O}_3$ ,  $\text{ThO}_2 - \text{UO}_2$  solid solutions and

Zr<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> modifications (Alamo & Roy, 1984) have been prepared by this method. The sol-gel technique has also become important for the preparation of noncrystalline solids (Scholze, 1984).

### 3.2.2 Chemical methods

There have been significant attempts to overcome the limitations of the ceramic method, resulting in alternative routes for solid state synthesis. The new methods, which rely on the knowledge of the structural chemistry and the reactivity patterns of solids, have not only enabled the synthesis of known solids in a state of high purity and homogeneity at far lower temperatures than by the conventional methods, but, in addition, have resulted in the synthesis of new phases. Among these alternative strategies, the following three methods have proved significant: the solid state precursor method and methods based on topochemical redox reactions and topochemical ion-exchange reactions. The emphasis in all three methods is in achieving the synthesis at low temperatures so that the products obtained are in a finely divided state with large surface areas – a feature essential for catalysis and other applications. More importantly, synthesis at temperatures considerably lower than the sintering temperatures of solids preserves the essential features of the parent structure with minimal structural reorganization (topochemical methods). Synthesis by topochemical methods often yields metastable phases that cannot be obtained by conventional methods.

The ideal condition for carrying out a solid state reaction in order to obtain a homogeneous product in the shortest time at the lowest possible temperature is to ensure homogeneous mixing of the reactants on an atomic scale. This, however, cannot be achieved in the ceramic method or its modifications. The only way to achieve this is to prepare a single phase (a chemical compound) in which the reactants are present in the required stoichiometry. Such a solid phase, called a *precursor*, on heating gives the desired product in a stoichiometric and homogeneous state. The *precursor method* has been employed for the synthesis of ternary oxides (Wold, 1980). Spinel-type ferrites, MFe<sub>2</sub>O<sub>4</sub> (M = Mg, Mn, Co, Ni), have been prepared by thermal decomposition of acetate precursors of the general formula M<sub>3</sub>Fe<sub>6</sub>(CH<sub>3</sub>COO)<sub>17</sub>O<sub>3</sub>OH.12C<sub>3</sub>H<sub>5</sub>N. The advantage of this method is that the precursors can be prepared as crystalline solids in a stage of high purity, possessing the desired M/Fe ratio. Moreover, the products are homogeneous and formed at fairly low temperatures. Other examples of synthesis of metal oxides through the compound precursor route are preparation of chromites, MCr<sub>2</sub>O<sub>4</sub>, by the decomposition of dichromates, (NH<sub>4</sub>)<sub>2</sub>M(CrO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, prepara-

tions of BaTiO<sub>3</sub> and LiCrO<sub>2</sub> by the decomposition of Ba[TiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>] and Li[Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] and of LaFeO<sub>3</sub> by the decomposition of La[Fe(CN)<sub>6</sub>]. Another example is the synthesis of ceramic oxides by the hydrolysis of metal alkoxides.

It is not always possible to find suitable single precursor compounds for the synthesis of all the desired compositions, because the stoichiometry of the precursor may not correspond to that of the product. Recently, a solid-solution precursor method which retains all the advantages of single compound precursors has been described (Horowitz & Longo, 1978; Longo & Horowitz, 1981; Vidyasagar *et al.*, 1984, 1985). The strategy is to make use of isostructural compounds containing a common anion so that they form a continuous series of solid solutions. The method has been used for the synthesis of several ternary oxides in the Ca–Mn–O system, such as Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>, CaMn<sub>3</sub>O<sub>6</sub>, CaMn<sub>4</sub>O<sub>8</sub> and CaMn<sub>7</sub>O<sub>12</sub> by the thermal decomposition of carbonate solid solutions, Ca<sub>1-x</sub>Mn<sub>x</sub>CO<sub>3</sub>, of calcite structure. Ca<sub>1-x</sub>Fe<sub>x</sub>CO<sub>3</sub> has been used to prepare unusual ferrites; Ca<sub>2</sub>Fe<sub>2-x</sub>Mn<sub>x</sub>O<sub>5</sub> with three types of transition metal–oxygen polyhedra have also been prepared in this manner. The method has been extended to hydroxide, oxalate and nitrate precursor solid solutions. Using hydroxides of the La(OH)<sub>3</sub> structure, compounds like LaNiO<sub>3</sub> and quaternary oxides have been prepared. Using nitrate precursors, BaPbO<sub>3</sub>, Ba<sub>2</sub>PbO<sub>4</sub> and BaSrPbO<sub>4</sub> have been prepared. Solid solution precursors have several advantages: (i) The reacting cations are uniformly blended together, thereby avoiding diffusion problems (the diffusion distance in this method is ~10 Å) and compositional inhomogeneities in the final product. (ii) The final product is formed at a much lower temperature than in a conventional ceramic synthesis, thus permitting an examination of subsolidus regions of the phase diagram which would otherwise be inaccessible. The products formed at lower temperatures will have large specific surface areas, which is an important requirement in catalyst preparations. The solid solution precursor method has been used for the low-temperature synthesis of Mo–W alloys (Cheetham, 1980) by hydrogen reduction of (NH<sub>4</sub>)<sub>6</sub>[Mo<sub>7-x</sub>W<sub>x</sub>O<sub>44</sub>].

*Vapour phase decomposition* of precursors at relatively low temperatures has been employed to produce solids. Thus SiC is formed by the decomposition of CH<sub>3</sub>SiH<sub>3</sub> or (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub>, while Si<sub>3</sub>N<sub>4</sub> is produced by the reactive decomposition of SiCl<sub>4</sub> or SiH<sub>4</sub> and NH<sub>3</sub>. Sialon powders are made by the reaction of metakaolin with NH<sub>3</sub> vapour. Transition metal sulphides are prepared by the reaction of precursor oxides, sulphates and chlorides with H<sub>2</sub>S or CS<sub>2</sub>. Pyrochlores of the type Pb<sub>2</sub>[Ru<sub>2-x</sub>Pb<sub>x</sub><sup>4+</sup>]O<sub>7-y</sub> and Bi<sub>2</sub>[Ru<sub>2-x</sub>Bi<sub>x</sub><sup>5+</sup>]O<sub>7-y</sub> are prepared by a

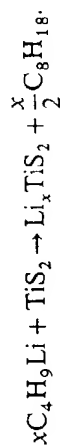
*Deintercalation* of lithium has also been done both electrochemically and chemically. Deintercalation of lithium from  $\text{LiMX}_n$  using mild oxidizing agents such as  $\text{I}_2/\text{CH}_3\text{CN}$  and  $\text{Br}_2/\text{CHCl}_3$  offers a low-temperature route for the synthesis of  $\text{Li}_x\text{MX}_n$  and  $\text{MX}_n$  phases that are otherwise impossible to prepare, such as  $\text{Li}_x\text{VS}_2$  and  $\text{Li}_x\text{VO}_2$ . Similarly  $\text{Mo}_6\text{S}_8$  can be prepared by acid leaching of  $\text{Cu}_x\text{Mo}_6\text{S}_8$  (Chevrel *et al.*, 1974). In Table 3.4 we list representative examples of lithium intercalation and deintercalation. From the table, it is seen that lithium intercalation occurs in a wide variety of oxide and sulphide hosts possessing one-, two-, and three-dimensional structures. In most cases, the gross structural features of the host are retained. In some cases, there are specific structural changes which can be accounted for within the framework of a topochemical mechanism, e.g.  $\text{LiReO}_3$  and  $\text{Li}_2\text{ReO}_3$  (Cava *et al.*, 1982). In both  $\text{LiReO}_3$  and  $\text{Li}_2\text{ReO}_3$ , the  $\text{ReO}_3$  host undergoes significant change on lithium insertion without breaking bonds. The 12-coordinated cavities in the  $\text{ReO}_3$  framework each become two octahedral cavities which are occupied by lithium. Lithium insertion in close-packed oxides such as  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Mn}_3\text{O}_4$  and  $\text{TiO}_2$  results in interesting structural changes. Lithium insertion changes the anion array of  $\text{Fe}_2\text{O}_3$  from hexagonal to cubic close packing. Lithium insertion suppresses the cooperative Jahn-Teller distortion of  $\text{Mn}_3\text{O}_4$ . Lithium inserted anatase,  $\text{Li}_{0.5}\text{TiO}_2$ , transforms to the superconducting spinel  $\text{LiTi}_2\text{O}_4$  around 770 K. Deintercalation of lithium by electrochemical methods or with iodine from  $\text{Li}_2\text{FeS}_2$  leads reversibly to  $\text{LiFeS}_2$ , which has the  $\text{LiTiS}_2$  structure.

Intercalation of sodium and potassium differs from that of lithium. In layered  $\text{A}_x\text{MX}_n$ , lithium is always octahedrally coordinated, while sodium and potassium occupy octahedral or trigonal prismatic sites; octahedral coordination is favoured by large values of  $x$  and low formal oxidation states of M. For smaller  $x$  and larger oxidation states of M, the coordination of sodium or potassium is trigonal prismatic. Intercalated caesium in  $\text{MX}_n$  is always trigonal prismatic. Intercalation of sodium and potassium in layered  $\text{MX}_2$  oxides and sulphides results in structural transformations involving a change in the sequence of anion layer stacking.

A number of inorganic solids having layered or a three-dimensional network structure exhibit fast cation transport. Sodium  $\beta$ - and  $\beta''$ -aluminas are typical examples. Sodium ions in these solids move rapidly in layers which provide a number of empty sites and easy pathways for ionic motion. Diffusion coefficients are typically of the order of  $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ . Fast cation conductors such as  $\beta$ -aluminas are good ion-exchangers. The exchange can be carried out easily at room temperature

low-temperature method employing strongly alkaline media (Horowitz *et al.*, 1981). The high-temperature phase ( $> 1300 \text{ K}$ ) of  $\text{ZrO}_2$  is obtained at room temperature by the hydrolysis of zirconium salts. The cubic ( $\delta$ ) form of  $\text{Bi}_2\text{O}_3$  can be stabilized at room temperature by incorporating additives such as  $\text{Y}_2\text{O}_3$  and  $\text{WO}_3$ .  $\gamma\text{-Fe}_2\text{O}_3$  is obtained by the dehydration of  $\gamma\text{-FeOOH}$  by organic bases (Desiraju & Rao, 1982). *Fused salt electrolysis* (Banks & Wold, 1974) is employed to synthesize oxides such as blue Mo bronzes.

Transition metal oxides and chalcogenides,  $\text{MX}_n$  (M = metal), possessing layered or chain structures can be intercalated at room temperature with lithium and other alkali metals to give the reduced phases,  $\text{A}_x\text{MX}_n$  (A = Li, Na or K). Formation of such phases was first reported by Rüdorff (1959). The process has several features which make it attractive both as a preparative technique and for the application of the phases as battery cathodes (Murphy & Christian, 1979): (i) the reaction is reversible and can be brought about chemically or electrochemically; (ii) the reaction is topochemical in nature, occurring with minimal structural reorganization of the host,  $\text{MX}_n$ , and (iii) A cations as well as electrons transferred to the host possess considerable mobility in  $\text{A}_x\text{MX}_n$  phases, rendering them mixed ionic-electronic conductors. It is this last feature that makes them useful as cathode materials in solid state batteries. The best known example of alkali metal intercalation is that of lithium into  $\text{TiS}_2$  to give  $\text{Li}_x\text{TiS}_2$  ( $0 < x \leq 1.0$ ) (Whittingham, 1978; Whittingham & Chianelli, 1980). The intercalation can be carried out by two methods. In the first, a chemical reagent, *n*-butyllithium dissolved in a hydrocarbon solvent. Such as hexane, is employed as the lithiating agent:



The second method for synthesizing lithium intercalates involves electrochemical reduction of  $\text{TiS}_2$ . A polycrystalline sample of  $\text{TiS}_2$  bonded into an electrode form is immersed in a polar organic solvent (e.g. dioxolane) in which lithium chloride (VII) is dissolved. A sheet of lithium metal of LiAl serves as the anode. On shorting the two electrodes, lithium ions intercalate  $\text{TiS}_2$ , the charge-compensating electrons passing through the external circuit. Electrochemical intercalation is particularly advantageous because the rate of the reaction can be controlled by imposing an external voltage across the cell; when the voltage exceeds the value corresponding to the free energy change  $\Delta G$  of the intercalation reaction, the reverse reaction – namely deintercalation – occurs.

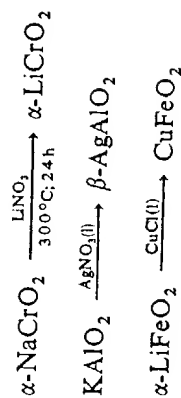
*Intercalation* of lithium has been achieved in a variety of  $\text{MX}_n$  hosts.

Table 3.4 Intercalation and deintercalation of lithium into  $MX_n$  hosts

$MX_n$ host	Remarks	References
$TiS_2$	$Li_xTiS_2$ ; $0 < x \leq 1$ . Phase is homogeneous over the composition	Whittingham (1978)
$VS_2$	$Li_xVS_2$ ; $0 < x \leq 1$ . Phases obtained by deintercalation of lithium from $LiVS_2$ using $I_2/CH_3CN$ . Three different phase regions: $0.25 \leq x \leq 0.33$ ; $0.48 \leq x \leq 0.62$ and $0.85 \leq x \leq 1$ apart from $VS_2$	Murphy <i>et al.</i> (1977)
$NbS_2(3R)$	$Li_{0.5}NbS_2$ and $Li_{0.70}NbS_2$	Whittingham (1978)
$TiS_3$	$Li_2TiS_3$ and $Li_{2+x}TiS_3$ ( $0 < x \leq 1$ )	Whittingham (1978)
$MoS_3$	$Li_xMoS_3$ ( $0 < x \leq 4$ )	Jacobson <i>et al.</i> (1979)
$MO_2$ (rutile)	$Li_xMO_2$ ( $x \geq 1$ ) ( $M = Mo, Ru, Os$ or $Ir$ )	Murphy <i>et al.</i> (1978)
$TiO_2$ (anatase)	$Li_xTiO_2$ ( $0 < x \leq 0.7$ ). $Li_{0.5}TiO_2$ transforms irreversibly to $LiTi_2O_4$ spinel at $500^\circ C$	Murphy <i>et al.</i> (1982)
$CoO_2$	$Li_xCoO_2$ ( $0 < x < 1$ ): Phases obtained by electrochemical delithiation of $LiCoO_2$	Mizushima <i>et al.</i> (1980)
$VO_2$	$Li_xVO_2$ ( $0 < x < 1$ ): Phases obtained by chemical delithiation of $LiVO_2$ using $Br_2/CHCl_3$	Vidyasagar & Gopalakrishnan (1982)
$VO_2(B)$	$Li_xVO_2$ ( $0 < x < 2/3$ ): Chemical lithiation using <i>n</i> -butyl lithium	Murphy & Christian (1979)
$Fe_2O_3$	$Li_xFe_2O_3$ ( $0 < x < 2$ ): Anion array transforms from hcp to ccp on lithiation	Thackeray <i>et al.</i> (1982)
$Fe_3O_4$	$Li_xFe_3O_4$ ( $0 < x < 2$ ): $Fe_2O_4$ subarray of the spinel structure remains intact	Thackeray <i>et al.</i> (1982)
$Mn_3O_4$	$Li_xMn_3O_4$ ( $0 < x < 1.2$ ): Lithium insertion suppresses tetragonal distortion of $Mn_3O_4$	Thackeray <i>et al.</i> (1983)
$MoO_3$	$Li_xMoO_3$ ( $0 < x < 1.55$ )	Dickens & Pye (1982)
$V_2O_5$	$Li_xV_2O_5$ ( $0 < x < 1.1$ ): Intercalation of lithium by using $LiI$	Dickens <i>et al.</i> (1979)
$ReO_3$	$Li_xReO_3$ ( $0 < x \leq 2$ ): Three phases $0 < x \leq 0.35$ ; $x = 1$ and $1.8 \leq x \leq 2$	Murphy <i>et al.</i> (1981) Cava <i>et al.</i> (1982)

both in aqueous and molten salt conditions. Thus, sodium  $\beta$ -alumina has been exchanged with  $H_3O^+$ ,  $NH_4^+$  and other monovalent and divalent cations, giving rise to different  $\beta$ -aluminas (Farrington & Briant, 1978; Tofield, 1982). Ion-exchange in inorganic solids is a general phenomenon, not restricted to fast ion conductors alone. The kinetic and thermodynamic aspects of ion-exchange in inorganic solids have been examined by England *et al.* (1983). Their results reveal that ion-exchange is quite a widespread phenomenon, occurring even when the diffusion coefficients are as small as  $\sim 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ , at temperatures far below the sintering temperatures of solids. Ion-exchange can occur at a considerable rate even in stoichiometric solids; mobile ion vacancies (introduced by nonstoichiometry or doping) are not required. Since the exchange occurs topochemically, it enables preparation of metastable phases that are inaccessible by high-temperature reactions.

England *et al.* (1983) have shown that a variety of metal oxides having layered, tunnel or close-packed structures can be ion-exchanged in aqueous solutions or molten salt media to produce new phases. Typical examples are:



The structure of the framework is largely retained during the exchange except for minor changes to accommodate the structural preferences of the incoming ion. Thus, when  $\alpha\text{-LiFeO}_2$  is converted to  $\text{CuFeO}_2$  by exchange with molten  $\text{CuCl}$ , the structure changes from that of  $\alpha\text{-NaCrO}_2$  to that of delafossite to provide a linear anion coordination for  $\text{Cu}^+$ . Similarly when  $\text{KAlO}_2$  is converted to  $\beta\text{-AgAlO}_2$  by ion-exchange, there is a structure change from cristobalite-type to ordered wurtzite-type. The change probably occurs to provide a tetrahedral coordination for  $\text{Ag}^+$ . An interesting ion-exchange reaction reported by Rice & Jackel (1982) is the conversion of  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  to  $\text{HNbO}_3$  and  $\text{HTaO}_3$ , respectively, by treatment with hot aqueous acid. The exchange of  $\text{Li}^+$  by protons is accompanied by a topotactic transformation of the rhombohedral  $\text{LiNbO}_3$  structure to the cubic perovskite structure of  $\text{HNbO}_3$ . The mechanism suggested for the transformation is the reverse of the transformation of cubic  $\text{ReO}_3$  to rhombohedral  $\text{LiReO}_3$  and  $\text{Li}_2\text{ReO}_3$  (Cava *et al.*, 1982), involving a twisting of the octahedra along the [111] cubic direction so as to convert the 12-coordinated perovskite tunnel sites to two 6-coordinated sites in the rhombohedral structure. Another interesting structural change accompanied by ion-exchange is

reported in  $\text{Na}_{0.7}\text{CoO}_2$  by Delmas *et al.* (1982). In  $\text{Na}_{0.7}\text{CoO}_2$ , the anion layer sequence is ABBA; cobalt ions occur in alternate interlayer octahedral sites and sodium ions in trigonal prismatic coordination in between the  $\text{CoO}_2$  units. When this material is ion-exchanged with LiCl, a metastable form of  $\text{LiCoO}_2$  with the layer sequence ABCBA is obtained. The phase transforms irreversibly to the stable  $\text{LiCoO}_2$  (ABCBC) around 520 K.

A variety of inorganic solids has been exchanged with protons to give new phases, some of which exhibit high protonic conduction; typical of them are  $\text{HTaWO}_6 \cdot \text{H}_2\text{O}$  (Groult *et al.*, 1982),  $\text{HMO}_3 \cdot x\text{H}_2\text{O}$  ( $M = \text{Sb}$ ,  $\text{Nb}$ ,  $\text{Ta}$ ) pyrochlores (Chowdhry *et al.*, 1982) and  $\text{HTiNbO}_3$  layer phase (Rebbah *et al.*, 1982). Ion-exchange has also been reported in metal sulphides. For example,  $\text{KFeS}_2$  undergoes topochemical exchange of potassium in aqueous solutions with alkaline earth metal cations to give new phases in which the  $[\text{FeS}_{4/2}]_\infty$  tetrahedral chain is preserved (Boller, 1978).

### 3.2.3 High pressure methods

The use of high pressure for solid state synthesis has acquired special significance after the synthesis of diamond by the General Electric Co. in 1955. Early investigations in this area were concerned with pressure-temperature phase diagrams of elements like Si, Ge and Bi. With the development of high-pressure technology, commercial equipment permitting simultaneous use of both high-pressure and high-temperature conditions have become available since the 1960s. Reviews presenting the experimental aspects and research progress in this area are available (Goodenough *et al.*, 1972; Joubert & Chenavas, 1975; Pistorius, 1976).

Experimental facilities required for high pressure synthesis may be divided into two major categories depending on the range of pressures involved. For the 1–10 kbar pressure range, the *hydrothermal method* is often employed. In this method, the reaction is carried out either in an open or a closed system. In the open system, the solid is in direct contact with the reacting gases ( $\text{F}_2$ ,  $\text{O}_2$  or  $\text{N}_2$ ) which also serve as pressure-intensifiers. Normally, a gold container is used in this type of synthesis. The method has been used for the synthesis of transition metal compounds such as  $\text{RhO}_2$ ,  $\text{PtO}_2$  and  $\text{Na}_2\text{NiF}_6$  where the transition metal is in a high oxidation state. Hydrothermal high pressure synthesis under closed system conditions has also been used for the preparation of higher-valence metal oxides; here, an internal oxidant like  $\text{KClO}_3$  is added to the reactants, which on decomposition under reaction conditions provides the necessary oxygen pressure. For example, oxide pyrochlores of palladium(IV) and platinum(IV),  $\text{Ln}_2\text{M}_2\text{O}_7$ , have been

prepared by this method (970 K, 3 kbar).  $(\text{H}_3\text{O})\text{Zr}_2(\text{PO}_4)_3$  (Subramanian *et al.*, 1984) and a family of zero thermal expansion ceramics (e.g.  $\text{Ca}_{0.5}\text{Ti}_2\text{P}_3\text{O}_{12}$ ) (Roy *et al.*, 1984) have also been prepared hydrothermally.

Zeolites are generally prepared under hydrothermal conditions in the presence of alkali (Barrer, 1981). The alkali, the source of silicon and the source of aluminium are mixed in appropriate proportions and heated (often below 370 K). A common reactant mixture is a hydrous gel composed of an alkali (alkali or alkaline earth metal hydroxide, organic quaternary bases, etc.), fresh  $\text{Al}(\text{OH})_3$  and silica sol or alkali, soluble aluminate, and silica sol. Under alkaline conditions, Al is present as  $\text{Al}(\text{OH})_4^-$  anions. The  $\text{OH}^-$  ions act as mineralizing catalyst while the cations present in the reactant mixture determine the kinds of zeolite formed. Besides water, some inorganic salts are also encapsulated in some zeolites. Zeolitization in the presence of organic bases has been developed and this route is useful for synthesizing silica-rich zeolites. Silicalite with a tetrahedral framework enclosing a three-dimensional system of channels (defined by 10 rings wide enough to absorb molecules up to 0.6 nm in diameter) has been synthesized by the reaction of tetrapropylammonium (TPA) hydroxide and a reactive form of silica between 370 and 470 K. The precursor crystals have the composition  $(\text{TPA})_2\text{O} \cdot 48\text{SiO}_2 \cdot \text{H}_2\text{O}$  and the organic cation is removed by chemical reaction or thermal decomposition to yield microporous silicalite which may be considered to be a new polymorph of  $\text{SiO}_2$  (Flanigen *et al.*, 1978). The clathrasil (silica analogue of a gas hydrate), dodecasil-1H, is prepared from an aqueous solution of tetramethoxysilane and  $\text{N}(\text{CH}_3)_4\text{OH}$ ; after the addition of aminoadamantane, the solution is treated hydrothermally under nitrogen for four days at 470 K (Groenen *et al.*, 1983).

Pressures in the range 10–150 kbar are commonly used for solid-state synthesis and such pressures are attained with three different kinds of apparatus. (i) In the *piston-cylinder apparatus* (Fig. 3.1), consisting of a

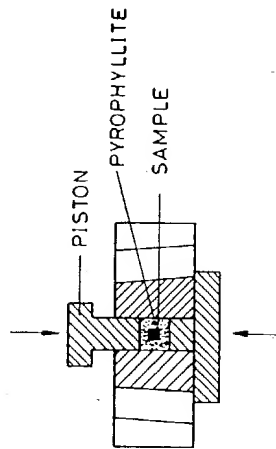
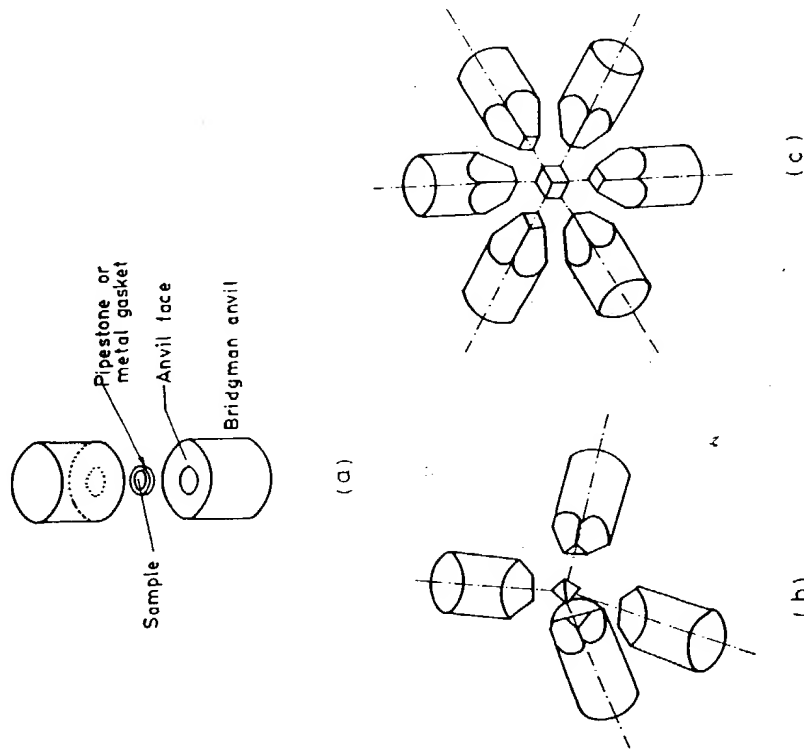


Figure 3.1. Piston-cylinder apparatus.



tungsten carbide chamber and a piston assembly, the sample is contained in a suitable metal capsule surrounded by a pressure-transducer (pyrophyllite). Pressure is generated by moving the piston through the blind hole in the cylinder. An internal microfurnace made of graphite or molybdenum can be incorporated in the design. Pressures up to 50 kbar and temperatures up to 1800 K are readily reached in a volume of 0.1 cm<sup>3</sup> using this design. (ii) In the *anvil apparatus* (Fig. 3.2), first designed by Bridgman, the sample is subjected to pressure by simply squeezing it between two opposed anvils. Massive support to the anvils is provided by the surrounding rings. Although pressures of ~200 kbar and temperatures up to 1300 K can be reached in this technique, it is not popular for solid-state synthesis since only milligram quantities can be handled. An extension of the opposed anvil principle is the tetrahedral

Figure 3.2. Anvil designs: (a) opposed anvil; (b) tetrahedral anvil; and (c) cubic anvil.

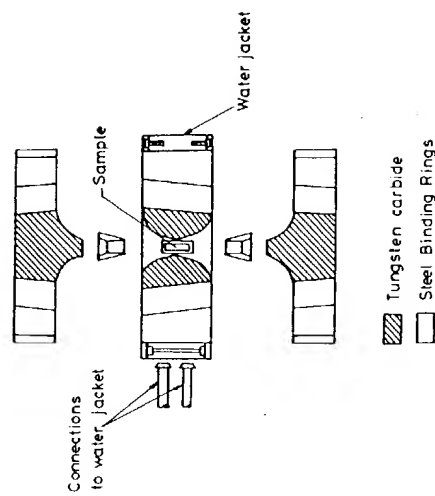


anvil design, where four massively supported anvils disposed tetrahedrally ram towards the centre where the sample is located in a pyrophyllite medium together with a heating arrangement. The multi-anvil design has been extended to cubic geometry, where six anvils act on the faces of a pyrophyllite cube located at the centre. (iii) The *'belt' apparatus* (Fig. 3.3) provides probably the most successful high pressure-high temperature combination for solid-state synthesis. This apparatus, which has been used for the synthesis of diamonds in the US is in a way a combination of the piston-cylinder and the opposed anvil designs; massive support is provided to the anvil as well as the cylinder. The apparatus consists of two conical pistons made of tungsten carbide, which ram through a specially shaped chamber from opposite directions. The chamber and pistons are laterally supported by several steel rings making it possible routinely to reach fairly high pressures (~150 kbar) and high temperatures (~2300 K).

In the *'belt' apparatus*, the sample is contained in a noble metal capsule (a BN or MgO container is used for chalcogenides) and surrounded by pyrophyllite and a graphite sleeve, the latter serving as an internal heater. In a typical high-pressure run, the sample is loaded, the pressure raised to the desired value and then the temperature increased. After holding the pressure for about 30 minutes, the sample is quenched (400 K s<sup>-1</sup>) while still under pressure. The pressure is then released after the sample has cooled to room temperature.

High-pressure research requires suitable calibration and measurement of pressures. Calibration is carried out by making use of standard

Figure 3.3. The belt apparatus.



substances which are known to undergo structure transitions at definite pressures.

Solids generally undergo transformations at high pressures to more close-packed structures, with an increase in coordination number. For example, on application of pressure, Si and Ge transform from a four- to a six-coordinated (white tin) structure, iron transforms from an eight- to a twelve-coordinated structure, while NaCl goes to the CsCl structure. The simple rule that high pressures result in lower volume and higher coordination number is based on the hard sphere model, which assumes constant radius and compressibility for atoms in different structures. The only generalization we can make is that pressure-induced transitions proceed in the direction of greater packing efficiency; less efficiently packed structures have a greater probability of undergoing pressure-induced structural changes. Pressure-induced phase transitions of solids may be quenchable or nonquenchable. Many high pressure forms of solids can be retained under ambient conditions as metastable phases, a typical case being that of diamond (quenchable). In general, transformations belonging to the reconstructive type, involving breaking and making of bonds, can be quenched; transformations involving only a slight movement of atoms are difficult to quench. This is the case with the monoclinic-tetragonal transition of  $\text{ZrO}_2$ , as also the tetragonal (red  $\text{PbO}$  type)-wurtzite transition of  $\text{SnO}$ . A large class of materials having quenchable high-pressure phases is the class of perovskite-related polytypes of  $\text{ABX}_3$  ( $X = \text{F}, \text{O}$ ) compositions (Goodenough *et al.*, 1972). In these cases, pressure has the effect of decreasing the tolerance factor,  $t$ , and hence stabilizing the cubic close-packing of the  $\text{AX}_3$  layers (B ion octahedra share corners) as against hexagonal close-packing (B ion octahedra share faces). In transition metal hydroxides,  $\text{MOOH}$ , the normal-pressure boehmite structure gives way to diaspor and  $\text{InOOH}$ -type structures at high pressures.

High-pressure methods have been used for the synthesis of new solids that cannot possibly be made otherwise. In general, the formation of a new compound from its components requires that the new composition has a lower free energy than the sum of the free energies of the components. Pressure can aid in the lowering of free energy in different ways (Goodenough *et al.*, 1972): (i) Pressure can delocalize outer  $d$  electrons in transition-metal compounds by increasing the magnitude of coupling between the  $d$  electrons on neighbouring cations, thereby lowering the free energy. Typical examples are provided by the synthesis of  $\text{ACrO}_3$  ( $A = \text{Ca}, \text{Sr}, \text{Pb}$ ) perovskites and  $\text{CrO}_2$ . (ii) Pressure can stabilize higher valence states of transition metals, thus promoting the formation of a new phase. For instance, in the  $\text{Ca-Fe-O}$  system only  $\text{CaFeO}_{2.5}$

(brownmillerite) is stable under ambient pressures. Under high oxygen pressures, iron is oxidized to the  $4^+$  state and hence  $\text{CaFeO}_3$  with the perovskite structure is formed. (iii) Pressure can suppress the ferroelectric displacement of cations and this aids the synthesis of new phases. The synthesis of  $\text{A}_x\text{MoO}_3$  bronzes, for example, requires populating the empty  $d$  orbitals centred on molybdenum; at ambient pressures,  $\text{MoO}_3$  is stabilized by a ferroelectric distortion of  $\text{MoO}_6$  octahedra up to the melting point. (iv) Pressure can alter site-preference energies of cations, thus facilitating the formation of new phases. For example, it is not possible to synthesize  $\text{A}^{2+}\text{Mn}^{4+}\text{O}_3$  ( $A = \text{Mg}, \text{Co}, \text{Zn}$ ) ilmenites because of the strong tetrahedral site preference of the divalent cations and one obtains a mixture of  $\text{A}[\text{A}(\text{Mn})\text{O}_4(\text{spinel}) + \text{MnO}_2(\text{rutile})]$  under atmospheric pressure instead of a single phase  $\text{AMnO}_3$ . However, the latter is formed at high pressures with a corundum-type structure in which both A and Mn ions are in octahedral coordination. (v) Pressure can suppress the  $6s^2$  core polarization in oxides containing  $\text{Tl}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$  isoelectronic cations. For example, a perovskite-type  $\text{PbSnO}_3$  cannot be made at atmospheric pressure because a mixture of  $\text{PbO} + \text{SnO}_2$  is more stable than a perovskite.

Stabilization of unusual oxidation states and spin states of transition metals is of considerable interest (e.g.  $\text{La}_2\text{Pd}_2\text{O}_7$ ). Such stabilization can be rationalized by making use of correlations of structural factors with the electronic configuration. Six-coordinated high-spin iron(IV) has been stabilized in  $\text{La}_{1.5}\text{Sr}_{0.5}\text{Li}_{0.5}\text{Fe}_{0.5}\text{O}_4$ , which has the  $\text{K}_2\text{NiF}_4$  structure (Demazeau *et al.*, 1982a). The elongated  $\text{FeO}_6$  octahedra and the presence of ionic Li—O bonds resulting from the  $\text{K}_2\text{NiF}_4$  structure favour the high-spin Fe(IV) state. The Li and Fe ions in this oxide are ordered in the  $ab$ -plane as evidenced by supercell spots in the electron diffraction pattern. Such an oxide is prepared under oxidizing conditions.  $\text{CaFeO}_3$  and  $\text{SrFeO}_3$  prepared under oxygen pressure also contain octahedral Fe(IV); while Fe(IV) in  $\text{SrFeO}_3$  is in the high-spin state with the  $e_g$  electron in the narrow  $\sigma^*$  band down to 4K, Fe(IV) in  $\text{CaFeO}_3$  disproportionates to Fe(III) and Fe(V) below 290 K (Takano & Takeda, 1983).  $\text{La}_2\text{LiFeO}_6$  prepared under high oxygen pressure has the perovskite structure with the iron in the pentavalent state (Demazeau *et al.*, 1982a).

Nickel in the  $3+$  state is present in the perovskite  $\text{LaNiO}_3$ , which can be prepared at atmospheric pressure; other rare earth nickelates can, however, be prepared at high oxygen pressures.  $\text{La}_2\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}_4$  and  $\text{MLaNiO}_4$  ( $M = \text{Sr}$  or  $\text{Ba}$ ) with the  $\text{K}_2\text{NiF}_4$  structure are other examples of oxides with Ni(III) (Demazeau *et al.*, 1982b).  $\text{MNiO}_{3-x}$  ( $M = \text{Ba}$  or  $\text{Sr}$ ) prepared under high pressure contain Ni(IV) as well (Takeda *et al.*,



1976). In  $\text{La}_2\text{Li}_{0.5}\text{Co}_{0.5}\text{O}_4$ , there is evidence for the transformation of the low-spin Co(III) to the intermediate- as well as high-spin states. The Li and Co ions are ordered in the *ab*-plane of this oxide of  $\text{K}_2\text{NiF}_4$  structure; the highly elongated  $\text{CoO}_6$  octahedra seem to stabilize the intermediate-spin state (Mohanram *et al.*, 1983). Intermediate-spin Co ions are reported to be formed in  $\text{Sr}_4\text{TaCoO}_8$  and  $\text{Sr}_4\text{NbCoO}_8$  as well. Oxides in perovskite and  $\text{K}_2\text{NiF}_4$  structures with trivalent Cu have been prepared under high oxygen pressure (Demazeau *et al.*, 1982b). High  $\text{F}_2$  pressure has been employed to prepare  $\text{Cs}_2\text{NiF}_6$  and other fluorides (Hagemuller, 1985).

As noted earlier, solid state reactions are generally slow under ordinary pressures even when the product is thermodynamically stable. Pressure has a marked effect on the kinetics of the reaction, reducing the reaction times considerably and at the same time resulting in more homogeneous and crystalline products. For instance,  $\text{LnFeO}_3$ ,  $\text{LnRhO}_3$  and  $\text{LnNiO}_3$  ( $\text{Ln} = \text{rare earth}$ ) are prepared in a matter of hours at high pressure – high temperature conditions, whereas under ambient pressures the reactions require several days ( $\text{LnFeO}_3$  and  $\text{LnRhO}_3$ ) or they do not occur at all ( $\text{LnNiO}_3$ ). In several  $(\text{AX})(\text{ABX}_3)_n$  series of compounds, the end members  $\text{ABX}_3$  and  $\text{A}_2\text{BX}_4$ , having the perovskite and  $\text{K}_2\text{NiF}_4$  structures respectively, are formed at atmospheric pressures but not the intermediate phases such as  $\text{A}_3\text{B}_2\text{X}_7$  and  $\text{A}_4\text{B}_3\text{X}_{10}$ . Pressure facilitates synthesis; for instance,  $\text{Sr}_3\text{Ru}_2\text{O}_7$  and  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$  are formed in 15 min at 20 kbar and 1300 K.  $\text{TaS}_3$ ,  $\text{NbSe}_3$  and such solids are prepared in 30 min at 2 GPa and 970 K.

### 3.2.4 Arc techniques

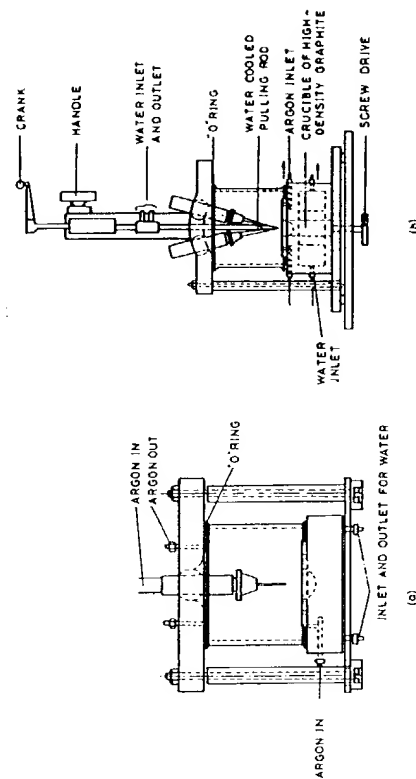
Use of the electric arc for the preparation of materials as well as growth of crystals of refractory solids has been reviewed by Loehman *et al.* (1969) and Müller-Buschbaum (1981). Basically, an arc for synthetic purposes is produced by passing a high current from a tungsten cathode to a crucible anode which acts as the container for the material to be synthesized (Fig. 3.4). The cathode tip is ground to a point in order to sustain a high current density. Typical operating conditions involve currents of the order of 70 amp at 15 volts. The arc is maintained in inert ( $\text{He}$ ,  $\text{Ar}$ ,  $\text{N}_2$ ) or reducing ( $\text{H}_2$ ) atmospheres. Even traces of oxygen attack the tungsten electrode and therefore the gases are freed from oxygen (by gettering with heated titanium sponge) before passing into the arc chamber. The arc can be maintained in an oxygen atmosphere using graphite electrodes instead of tungsten. The crucible (anode) is made from a cylindrical copper block and is water-cooled during operation.

For the synthesis of materials, the starting materials are placed in the copper crucible. An arc is struck by allowing the cathode to touch the

anode. The current is raised slowly while the cathode is simultaneously withdrawn so as to maintain the arc. The arc is then positioned so that it bathes the sample in the crucible. The current is increased until the reactants melt. When the arc is turned off, the product solidifies in the form of a button. Because of the enormous temperature gradient between the melt and the water-cooled crucible, a thin solid layer of the sample usually separates the melt from the copper hearth; in this sense, the sample forms its own crucible and hence contamination with copper does not take place. Contamination of the sample by tungsten vaporizing from the cathode can be avoided by using water-cooled cathodes. The arc method has been successfully used for the synthesis of various oxides of Ti, V and Nb. A number of lower-valence rare earth oxides,  $\text{LnO}_{1.5-x}$ , have been prepared by arc fusion of  $\text{Ln}_2\text{O}_3$  with Ln metal.

A sophisticated version of the arc method is the *triarc technique* (Fig. 3.4) developed by Fan & Reed (1972) for growing single crystals of high-melting solids. The main differences between the single and triarc furnace lie in the use of three symmetrically arranged thorated tungsten cathodes and a graphite crucible as anode, together with a water-cooled pulling rod. For crystal growth using the triarc furnace, the polycrystalline sample is loaded in the crucible, all the three arcs are struck simultaneously and the sample is brought to just-melting condition. The pulling rod is then lowered down until the tip just touches the melt. By slowly pulling the rod up, a 'neck' is formed between the frozen solid and the melt in the crucible. This is equivalent to using a single seed crystal in the conventional pulling technique for crystal growth. Careful driving of

Figure 3.4. (a) D.c. arc furnace; (b) Triarc.



the pulling rod while maintaining the triarc produces a single crystal boule. The method has been used to grow single crystals of  $\text{Ti}_3\text{O}_5$ ,  $\text{Ti}_2\text{O}_3$  and  $\text{NbO}$ .

A further modification of the arc method is the *arc transport (trans(er) technique* in which the material to be grown as a single crystal is transported by an electric arc. A vertical arc between the cathode (filled with the melt) and the anode carrying the seed crystal is kept at constant length by progressively raising the anode. The fused material is transported across the arc from cathode to anode where it grows on the seed crystal.  $\text{NiO}$  crystals have been prepared by this technique by using  $\text{Ni}$  electrodes (Honig & Rao, 1981).

### 3.2.5 Skull melting

This technique is useful not only for preparing metal oxides, but also for growing crystals of these oxides. The technique involves coupling of the material to a radio frequency electromagnetic field (200 kHz–4 MHz, 20–50 kW) (Harrison *et al.*, 1980). The material is placed in a container consisting of a set of water-cooled cold fingers set in a water-cooled base (all made of copper), the space between the fingers being large enough to permit penetration of the electromagnetic field into the interior, but small enough to avoid leakage of the melt. The process is crucibleless and a thin solid skull separates the melt from the water-cooled container. Single crystals of very large sizes can be grown by this method and the mass of the starting materials can be up to 1 kg. Temperatures up to 3600 K are reached in this technique, permitting growth of crystals of materials like  $\text{ThO}_2$  and stabilized  $\text{ZrO}_2$ . The stoichiometry of the oxide is readily controlled by the use of an appropriate ambient gas ( $\text{CO}/\text{CO}_2$  mixtures, air or oxygen). Large crystals of  $\text{CoO}$ ,  $\text{MnO}$  and  $\text{Fe}_3\text{O}_4$  have been grown by the skull method and the technique will undoubtedly find many applications in the future. In  $\text{CoO}$  and  $\text{MnO}$ , trivalent metal ions were eliminated by heating the crystals in an appropriate  $\text{CO}/\text{CO}_2$  mixture. Recently, crystals of  $\text{La}_2\text{NiO}_4$  and  $\text{Nd}_2\text{NiO}_4$  have been grown by the skull method.

### 3.2.6 Chemical vapour deposition (CVD)

Deposition of a solid on a substrate by means of a chemical reaction between vapours is called chemical vapour deposition (CVD). The process involves (i) the formation of reactants in the vapour state, (ii) transport of the vapour to the deposition region and (iii) deposition of the solid from the vapour. CVD has become an important technique in solid-state synthesis and finds application in the synthesis of a broad spectrum of solids ranging from amorphous and polycrystalline deposits

to epitaxial growth of single-crystal films used in devices (Tietjen, 1973). As a synthetic technique, CVD has several advantages. The method permits preparation of virtually any material in almost any geometry. Since product formation is not limited by kinetic factors and diffusion, it is possible to synthesize solids at relatively low temperatures; homogeneity and stoichiometry are also easily controlled. An additional advantage is that incorporation of selected dopants in controlled concentration during the synthesis is achieved.

CVD is widely used for the preparation of silicon and III–V semiconductors for device purposes. There are two different CVD processes for the preparation of silicon: (i) hydrogen reduction of  $\text{SiCl}_4$  and (ii) pyrolysis of  $\text{SiH}_4$ . The deposition is carried out either homoeopitaxially on silicon or on an insulating substrate such as sapphire. Several methods have been developed for the synthesis of III–V compounds. For example, GaAs is made by CVD using  $\text{AsCl}_3$  and Ga vapour in a hydrogen atmosphere; here,  $\text{AsCl}_3$  acts not only as the source of As but as the transporting agent for Ga as well. Another method for the synthesis of this class of compounds makes use of the reaction between a volatile hydride of a group V element with a group III element in the presence of  $\text{HCl}$  gas:



A third method makes use of hydrides of group V elements together with volatile organometallic compounds of group III elements such as trimethylgallium and trimethylaluminium.

Insulating materials such as  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$  and  $\text{Al}_2\text{O}_3$  have also been made by CVD methods.  $\text{Si}_3\text{N}_4$ , a high-temperature ceramic, is formed by the reaction of  $\text{NH}_3$  with  $\text{SiH}_4$  or  $\text{SiCl}_4$ . The reaction using  $\text{SiH}_4$  has the advantage that it occurs at lower temperatures. CVD has been particularly useful in the synthesis of superconducting and magnetic materials. One such material  $\text{Nb}_3\text{Si}$  is an important A15 superconductor. Preparation of this phase by the reaction of the elements at elevated temperatures yields only a nonsuperconducting phase which has the  $\text{Ti}_3\text{P}$  structure. It is only by deposition from vapours below 1120 K that the desired phase with the A15 structure is obtained. Rare earth garnets, useful as bubble-domain magnetic materials, have been prepared as single crystals by deposition from volatile metal halides.

### 3.2.7 Synthesis of organic solids

Synthesis is the main preoccupation of organic chemists and we can not possibly deal with the varied aspects of organic synthesis

here. Synthesis of organic solids exhibiting properties of interest to the solid state scientists however involves certain procedures which are noteworthy and we shall discuss a few typical systems of current interest. TTF-TCNQ and such donor-acceptor complexes and polyacetylene and other conducting organic polymers are areas of active study in solid state science today (Hatfield, 1979). Synthetic methods for the preparation of TTF, TCNQ and related donor and acceptor molecules are described in the literature (Narita & Pittman, 1976; Wheland & Martin, 1975). The charge transfer salts are usually prepared by mixing hot acetonitrile solutions of the donor and the acceptor. What is important for solid state chemistry is not the synthesis *per se* of these organic compounds, but the design of donors and acceptors so that the charge transfer solids possess the desired structure and properties. Certain guidelines based on molecular stacking, stoichiometry and degree of charge transfer have been evolved for the design of donor-acceptor complexes exhibiting metallic properties (Torrance, 1979). Thus, 1:1 charge transfer salts possessing uniform segregated stacking and incomplete charge transfer show metallic properties. There have been attempts to link the three factors to the molecular properties of donors and acceptors. Segregated stacking seems to be favoured when the donor-acceptor overlap is particularly weak. The degree of charge transfer is chiefly determined by the ionization energy of the donor (reduction potential of the cation). A plot of the room-temperature conductivity against the reduction potential of cation for the TCNQ family of donor-acceptor solids reveals that only in the narrow region of the reduction potential close to zero are the solids metallic. When the potential is too negative, complete charge transfer occurs giving ionic salts and when the potential is positive, neutral complexes are obtained (Torrance, 1979). Factors that determine the stoichiometry of donor-acceptor complexes are not definitely known. In the family of TTF-halide salts, the observed nonstoichiometries have been accounted for in terms of Madelung energy, showing that ionization potential of the donor and electron affinity of the acceptor are important factors determining stoichiometry.

Attempts have also been made to design one-dimensional organic superconductors based on donor-acceptor interaction (Bechgaard & Jerome, 1982). For this purpose it is necessary to avoid Peierls distortion, which results in the loss of metallic property (see Section 6.8). This is accomplished by preparing charge transfer complexes of selenium analogues of TTF such as TMTSF(Tetramethyltetraselenafulvalene). Charge transfer solids of the type TMTSF<sub>2</sub>X(X = ClO<sub>4</sub>, ReO<sub>4</sub>, PF<sub>6</sub> and AsF<sub>6</sub>) indeed show superconductivity, the perchlorate salt showing the

superconducting transition at 1.2 K and atmospheric pressure and the others at high pressures.

Polyacetylene, (CH)<sub>x</sub>, is the prototype of conducting organic polymers (Etemad *et al.*, 1982) whose electrical conductivity can be varied by doping over twelve orders of magnitude from that of an insulator ( $< 10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$ ) through semiconductor to a metal ( $> 10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$ ). Polyacetylene can be prepared by admitting acetylene gas into a glass reactor vessel whose inside wall has been wetted with a methylbenzene solution of (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Al and (n-C<sub>4</sub>H<sub>9</sub>O)<sub>4</sub>Ti Ziegler catalyst (Shirakawa & Ikeda, 1971; Shirakawa *et al.*, 1973). A cohesive film of polyacetylene grows on all surfaces which have been wetted by the catalyst solution. Polymerization at room temperature produces a mixture of 80% *cis* and 20% *trans* isomers. When the temperature is around 350 K, nearly 100% *cis*-(CH)<sub>x</sub> is produced; at 420 K (decane solvent) the product is 100% *trans*. The *cis-trans* isomerization occurs at ~470 K. As formed, (CH)<sub>x</sub> films consist of randomly oriented fibrils, each fibril being a few hundred angstroms in diameter. The room-temperature conductivity of (CH)<sub>x</sub> depends upon the *cis* and *trans* content, the value varying between  $10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$  for the *trans* polymer ( $E_g \sim 0.8 \text{ eV}$ ) and  $10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$  for the *cis* polymer ( $E_g \sim 1.0 \text{ eV}$ ). As a result of the large overall band width arising from the conjugated  $\pi$ -electrons, (CH)<sub>x</sub> is different from the common organic semiconductors made up of weakly interacting molecules (e.g. anthracene) or from saturated polymers with no  $\pi$ -electrons (e.g. polyethylene).

Like inorganic semiconductors, polyacetylene can be doped with a variety of donors and acceptors to give *n*-type or *p*-type semiconductors. Doping to high levels (above ~1%) results in a semiconductor-metal transition giving a new class of metals with a wide range of electro-negativity (MacDiarmid & Heeger, 1979; Mammone & MacDiarmid, 1984). Doping can be done chemically or electrochemically. Chemical doping can be done by exposure of the (CH)<sub>x</sub> film to a known vapour pressure of a volatile dopant, e.g. I<sub>2</sub>, AsF<sub>5</sub>, etc., until the desired conductivity is obtained. Removal of the dopant vapour essentially 'freezes' the conductivity at that stage. Doping can also be done by treatment of the polymer film with a solution of the dopant in an appropriate solvent (e.g. I<sub>2</sub> in pentane, sodium naphthalide in THF) or by treatment with molten Na or K. Polyacetylene can act as an electron-source or as an electron-sink according to whether it is oxidized (doped *p*-type) or reduced (doped *n*-type). (CH)<sub>x</sub> begins to lose electrons at an applied potential of +3.10 volts and gains electrons at an applied potential of +1.75 volts versus a Li/Li<sup>+</sup> electrode. Electrochemical

doping can be carried out by using strips of  $(\text{CH})_x$  as anode and cathode. For example, when the electrodes, immersed in a solution of  $\text{LiClO}_4$  in propylene carbonate, are connected to a d.c. source (4V), oxidation of  $(\text{CH})_x$  occurs at the anode giving  $[(\text{CH})^{\cdot+}(\text{ClO}_4^-)]_x$  and reduction occurs at the cathode giving  $[\text{Li}^+(\text{CH})^{\cdot-}]_x$ . The possibility of reversible redox reactions of polyacetylene in an electrochemical cell forms the basis of light weight, high power-density, rechargeable storage batteries (Nigrey *et al.*, 1981).

A number of polyheterocycles have been prepared. For instance, oxidative electrochemical polymerization of pyrrole produces polypyrrole, invariably containing dopant anions from the electrolyte. A polypyrrole film containing  $\text{AsF}_6^-$  of about  $10\text{ }\mu\text{m}$  thickness, is produced when a mixture of 0.2 M pyrrole and 0.004 M tetra-*n*-butylammonium hexafluoroarsenate in dimethyl sulphate is electrolysed using indium-tin oxide anode and platinum cathode at a current density of  $2\text{ mA cm}^{-2}$  for 20 minutes. The polymer grows on the indium-tin oxide surface (Hotta *et al.*, 1983). The doped polymers so obtained can be converted into neutral polymers by immediate reversal of the polarity after electrochemical polymerisation. Polythiophene and poly(3-methylthiophene) are prepared by similar methods. Organometallic polymers possessing high electrical conductivity have also been prepared (Sheats *et al.*, 1984).

### 3.3 Microcrystalline particles and clusters (the finite solid state)

There is a distinct region of small aggregates or clusters which falls between the atomic (or molecular) domain and that of condensed matter. These small particles and clusters possess unique properties and have several technological applications. The formation of these particles involves a vapour-solid, a liquid-solid, a solid-solid or a vapour-liquid-solid type of phase change governed by nucleation and it is important that the size of the growing nucleus is controlled (Muktani, 1981).

Microclusters of metals up to 500 atomic mass units (AMU) have been obtained by inert-gas vaporization-condensation; the metal vapour effuses from a hot cell through a narrow orifice. The mean particle size by this technique varies in the range 5–200 Å, the microclusters containing anywhere between 1 and 500 atoms (e.g.  $\text{Sb}_{1-500}$ ;  $\text{Bi}_{1-250}$ ). Mass spectroscopy has been used to determine sizes of such clusters. Granquist and Buhrman (1976) have described an apparatus to synthesize particles in the range 30–60 Å diameter. The arc-plasma method has been employed to prepare microclusters of ceramic

materials such as tungsten carbide (50–80 Å) and silicon carbide (100–200 Å). Biphasic ceramic-metal composites of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  or  $\text{ZrO}_2$  with Cu, Pt, Sn or Ni have been prepared by a sol-gel process (Roy & Roy, 1984). The xerogel consists of a microcrystalline or a noncrystalline ceramic matrix in which the metallic component is dispersed as small islands.

Microcrystals made up of relatively larger particles (still in the submicron range) are useful in applications involving solid state diffusion (or reaction) and sintering. These are synthesized by any of the following techniques: spray-dry, freeze-dry, sol-gel, pyrogel (high-temperature spray) or liquid drying. Thus, the freeze-dry technique has been used to prepare  $\alpha$ - and  $\gamma$ - $\text{Fe}_2\text{O}_3$  (150–200 Å) while the sol-gel technique has been used to prepare  $\text{Y}_3\text{Fe}_5\text{O}_{12}$  and  $\text{PbZr}_{0.32}\text{Ti}_{0.48}\text{O}_3$  (PZT). In all these techniques, one starts with aqueous solutions or mixed sols of the appropriate stoichiometry; the solutions are atomized and heat or mass transfer is achieved in milliseconds. The temperature of the sink (source) is around 300 K for sol-gelling (in a bath of 2-ethylhexanol and liquid drying in a bath of acetone), at 78 K for freeze-drying, around 600 K for spray-drying and around 1200 K for the pyrogel technique. The preparations enable homogeneity at molecular level, small grain size, low porosity, large surface area and theoretical density of sintered compacts.

Transmission and scanning electron microscopy are employed for a direct study of microclusters while the distribution of sizes (or average diameter) is provided by sedimentation and other techniques. The average particle diameter is obtained by the Brunauer-Emmett-Teller (BET) surface-area method and by X-ray line broadening.

Microcrystals exhibit properties distinctly different from those of bulk solids. The fractional change in lattice spacing has been found to increase with decreasing particle size in  $\text{Fe}_2\text{O}_3$ . Magnetic hyperfine fields in  $\alpha$ - $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  are lower in the microcrystalline phase compared to those of the bulk crystalline phases. The tetragonality (i.e. the departure of the axial ratio from unity) of ferroelectric  $\text{BaTiO}_3$  decreases with decrease in particle size; in PZT, the low-frequency dielectric constant decreases and the Curie temperature increases with decreasing particle size. The small particle size in microcrystals cannot apparently sustain low-frequency lattice vibrations.

### 3.4 Amorphous materials

It is only in recent years that there has been the realization that most materials can be rendered amorphous. Referring specifically to glasses, it may be said that most materials, if cooled fast enough (and far

enough) from the liquid state, can be made in the form of glasses. The various techniques available for the preparation of glasses (Angell, 1981, Elliott *et al.*, 1985) are cooling of supercooled liquid phases, vapour deposition, shock disordering, radiation disordering, desolvation and gelation (Fig. 3.5). All these techniques with the exception of the first produce materials which cannot easily be characterized, especially with regard to their entropies relative to those of the corresponding crystals.

A variety of glasses, possessing different types of bonding, have been prepared. In Table 3.5, we list a few of them along with their glass transition temperature to illustrate the universality of glass formation. The rate of cooling has to be very fast to prepare glasses from metallic materials; the temperature drop required is around 1000 degrees in a millisecond ( $\sim 10^5 \text{ K s}^{-1}$ ). Melt-spinning, where the metallic glass is spun off a copper rotor as a ribbon at a rate exceeding a kilometre per minute is employed for the purpose. Most other glasses prepared by quenching melts require slower rates;  $\text{SiO}_2$  requires a cooling rate of hardly  $0.1 \text{ K s}^{-1}$  and this is attained by allowing the melt to cool freely. *Splat-quenching* techniques with a range of cooling rates ( $10^5 - 10^8 \text{ K s}^{-1}$ ) have also been employed to prepare metallic glasses. Of special interest is the technique of *laser-glazing* where the surface of a crystalline material is made glassy by exposing it to a moving focussed laser beam so that the subjacent solid acts as heat sink; the quenching rate in this technique has been estimated at  $10^{11} \text{ K s}^{-1}$ .

The vapour deposition method is widely used to obtain amorphous solids. In this technique, atoms, molecules or ions of the substance (in

dilute vapour phase) are deposited on to a substrate maintained at a low temperature. Most vapour-deposited amorphous materials crystallize on heating, but some of them exhibit an intervening second-order transition (akin to the glass transition). Amorphous solid water and methanol show such transitions. The structural features of vapour-deposited amorphous solids are comparable to those of glasses of the same materials prepared by melt-quenching.

Disordering of crystalline materials by subjecting them to shock (e.g. as in the case of quartz and other minerals) or by large dosages of radiation (neutrons or alpha particles) also produces the amorphous state. The *metamict* form (Pabst, 1952) produced by irradiation is unstable with respect to the vitreous form. Substances such as magnesium acetate are rendered glassy by a desolvation process. In the gelation method, the material is first produced in gel form by hydrolysis of an organic derivative (e.g. ethyl silicate); the gel is then dried and collapsed into the glassy state.

Solid state reactions may also produce amorphous solids starting from crystalline solids. For instance, Yeh *et al.* (1983) have found that absorption of hydrogen by crystalline  $\text{Zr}_3\text{Rh}$  transforms it to a hydrided amorphous material.

### 3.5 Crystal growth

Crystals are essential both for fundamental studies of solids and for fabrication of devices. The ideal requirements are large size, high purity and maximum perfection (freedom from defects). It may also be

Figure 3.5. Various routes for preparing amorphous solids.

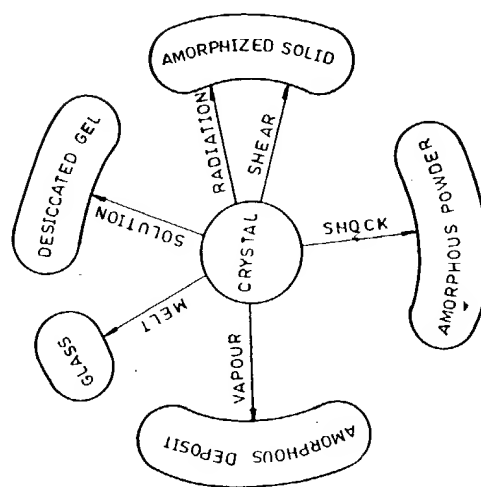


Table 3.5. Typical glassy amorphous solids

Substance	Nature of bonding	Glass transition, K
$\text{SiO}_2$	Covalent	1450
$\text{GeO}_2$	Covalent	820
$\text{As}_2\text{S}_3$	Covalent	470
Se	Covalent (Polymeric)	320
Polyvinylacetylene	Covalent (Polymer)	310
$\text{BeF}_2$	Ionic	570
$75\% \text{AgI} - 25\% \text{Ag}_2\text{SeO}_4$	Ionic	75
$\text{Au}_{0.8}\text{Si}_{0.1}\text{Ge}_{0.1}$	Metallic	295
Propylene carbonate	van der Waals	160
Isopentane	van der Waals	65
$\text{H}_2\text{O}$	Hydrogen bonded	139(?)
$\text{C}_2\text{H}_5\text{OH}$	Hydrogen bonded	90
$\text{Fe}_{80}\text{B}_{20}$	Metallic	crystallizes

necessary to incorporate selective impurities (dopants) during growth in order to achieve required electronic properties. A number of methods is available for growing crystals (Table 3.6) and the subject has been reviewed extensively in the literature (Laudise, 1970; Banks & Wold, 1974; Mroczkowski, 1980; Honig & Rao, 1981).

The most common methods of growing crystals involve solidification from the melt (in the case of one-component systems) or crystallization from solution. Some of the methods for growing crystals from melt are described schematically in Fig. 3.6. In the *Czochralski method*, commonly known as the pulling technique, the material is melted by induction or resistance heating in a suitable nonreactive crucible. The melt temperature is adjusted to slightly above the melting point and a seed crystal is dipped into the melt. After thermal equilibration is attained, the seed is slowly lifted from the melt. As the seed is pulled, continuous growth occurs at the interface. The diameter of the growing crystal can be controlled by adjusting the rate of pulling, the rate of melt-

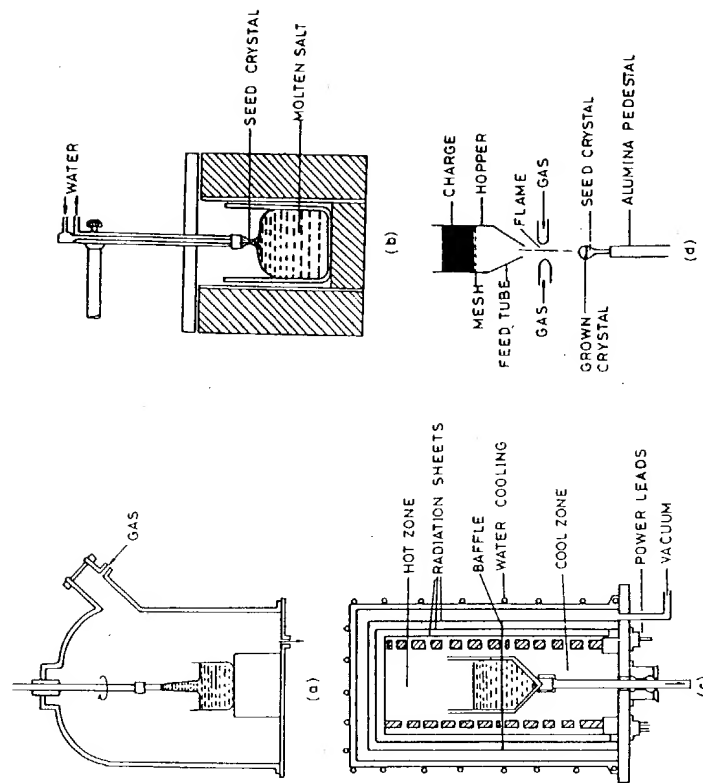
level drop and the heat fluxes into and out of the system. The technique has the advantage that the growth interface does not come into contact with the walls of the crucible and hence formation of unwanted nuclei is avoided. The method has been used for the growth of silicon, germanium, III-V semiconductors, ceramic oxides like  $\text{Al}_2\text{O}_3$ , rare earth perovskites such as  $\text{LnAlO}_3$ ,  $\text{LnFeO}_3$ , garnets, scheelites, etc. Oxide materials can be grown in air while others require closed systems and atmosphere control. In the triarc method (described earlier in Section 3.2.4) the crystal is pulled from the melt. The *Kyropoulos method* is similar to the Czochralski method, but instead of pulling the seed crystal, the crystal-liquid interface moves into the melt as crystallization proceeds. In the *Bridgman-Stockbarger method*, a sharp temperature gradient is provided across the melt which results in nucleation in the colder region. The conical geometry of the crucible at the bottom limits the number of nuclei formed.

Another method for growing crystals from melt is the *floating zone*

Table 3.6 Methods of Crystal growth

I. Growth in one-component systems	
(a) Solid-solid	Strain-annealing, devitrification or polymorphic phase change
(b) Liquid-solid	1. Directional solidification (Bridgman-Stockbarger)
	2. Cooled seed (Kyropoulos)
	3. Pulling (Czochralski and also triarc)
	4. Zoning (Horizontal zone, vertical zone)
	5. Flame fusion (Verneuil)
	6. Slow cooling in skull melter
(c) Gas-solid	Sublimation-condensation or sputtering
II. Growth involving more than one component	
(a) Solid-solid	Precipitation from solid solution
(b) Liquid-solid	1. Growth from solution (evaporation, slow cooling and temperature differential)
	(i) Aqueous solvent; (ii) Organic solvents; (iii) Molten solvents; (iv) Hydrothermal
	2. Growth by reaction
	(i) Chemical reaction; (ii) Electrochemical reaction
	3. Growth from melt; e.g. Congruently melting intermetallic compounds
(c) Gas-solid	1. Growth by reversible reaction (chemical vapour transport)
	2. Growth by irreversible reaction (epitaxial process).

Figure 3.6. Methods for crystal growth from melt: (a) Czochralski method; (b) Kyropoulos method; (c) Bridgman-Stockbarger method and (d) Verneuil method.





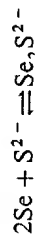
technique in which a section of the starting material, held vertically in the form of a rod, is melted by suitable heating. As the molten zone is moved along the rod, progressive melting of the sample at one end of the zone and crystal growth at the other end occur. If a seed crystal is provided at one end, the whole rod can be converted into a single crystal. The method has the advantage that there is no contamination from the crucible. The method is similar to purification by *zone-refining* and has been used routinely to grow single crystals of silicon. In the *flame fusion* (Verneuil) method, the powder sample is directly fed into an oxy-hydrogen flame and the melt allowed to drip on a seed crystal. As crystallization occurs on the top, the growing seed is lowered slowly, facilitating the growth of large crystals. The method has been used for the growth of high-melting oxides such as ruby and sapphire. A variant of the flame fusion technique is the *plasma torch method* in which the powder is dropped through a hot plasma generated and maintained by high-frequency current. The skull technique (see Section 3.2.5) has emerged to become a useful method for growing large crystals of several oxides.

Frequently, growth of crystals from melt involves more than one component, such as impurities, intentionally added dopants, etc., in addition to the major component. In these cases, it is essential to know the distribution of the second component between the growing crystal and the melt. This distribution occurs according to the phase diagram relating the equilibrium solubilities of the second component (impurity) in the liquid and the solid phases.

A number of crystal-growth methods making use of the solubility of a solute in a suitable solvent are known. Crystallization requires supersaturation, which can be provided by a temperature difference between the dissolution and growth zones, by solvent-evaporation or by a chemical reaction. In the solution methods, it is difficult to avoid contamination of the product by other components in the solution or flux. The flux technique has nevertheless been used to grow crystals of  $\text{GeO}_2$ ,  $\text{SiO}_2$ ,  $\text{BaTiO}_3$ ,  $\text{KTaO}_3$ ,  $\alpha\text{-Al}_2\text{O}_3$ ,  $\text{GdAlO}_3$  and so on. The role of the solvent is to depress the melting point of the solute to be grown as a crystal. Although supersaturation is required for crystal growth, experimentally it is found that growth rate from solution is enormously faster than expected, considerable growth occurring even at low degrees of supersaturation (1%). This discrepancy was explained by Frank and Cabrera in terms of the effect of dislocations on crystal growth. Whereas the growth of a perfect crystal requires nucleation of a new layer on a perfect surface after completion of the previous layer, in the presence of a screw dislocation, growth does not require nucleation of a new layer. The dislocation provides a stepped surface where growth can occur even at

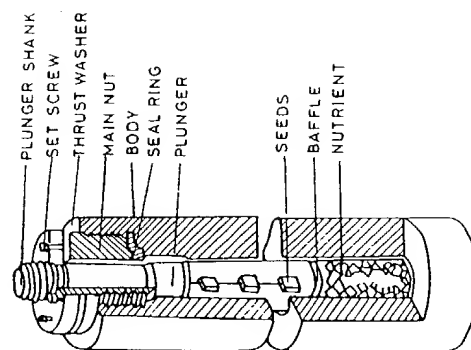
low degrees of supersaturation. Spiral growth patterns arising from screw dislocations have been observed on a number of crystals grown from solution and vapour supporting the Frank model.

Among the solution-growth methods, crystallization from aqueous solution is well known. Materials with low water solubility may be brought into solution by the use of complexing agents (mineralizers). Selenium, for instance, can be grown from aqueous sulphide solutions, by making use of the reaction



An important method for growth of crystals with low water solubility is the hydrothermal method discussed earlier in Section 3.2.3. Hydrothermal synthesis is generally carried out with an autoclave of the type shown in Fig. 3.7. The autoclave consists of a lower nutrient region and an upper growth region separated by a baffle. The solute is placed in the nutrient region and a few seed crystals are suspended in the growth region. The vessel is filled with water to a predetermined volume, mineralizers are added if necessary, then it is closed and the temperature raised while providing a gradient. Since the solubility of most substances increases with increasing temperature, the nutrient region is maintained at a higher temperature than the growth region. The solvent saturates at the dissolving zone, moves by convection to the cooler growth zone where it is supersaturated and deposits the solute on the seed crystal. The solution is undersaturated when it reaches the nutrient region, thus dissolving more solute and the cycle goes on. Large quartz

Figure 3.7. Apparatus for hydrothermal synthesis.

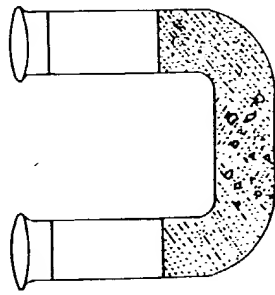


crystals are grown by this method. If the solute happens to have a retrograde solubility, as in the case of  $\text{AlPO}_4$ , the temperature gradient has to be reversed between the growth and the nutrient regions. In hydrothermal synthesis, the degree of filling the autoclave with solvent is an important factor; it has to be more than 32% in order to provide a high density of the solvent. Conventionally, hydrothermal experiments are carried out in alkaline medium, the  $\text{OH}^-$  ion acting as complexing agent. Hydrothermal synthesis has been used to stabilize unusual oxidation states in transition metal compounds and to synthesize low-temperature and metastable phases (Rabenau, 1985).

Insoluble ionic solids such as  $\text{CaCO}_3$  and  $\text{BaSO}_4$  cannot be grown by conventional solution methods or even by controlled chemical reaction because of instantaneous precipitation of the product when the reactants are mixed. The *gel method* is useful for the growth of such solids; this simple method depends on controlled diffusion of the reagents through the gel. A U-tube is filled with silica gel produced by acidifying a solution of sodium metasilicate (Fig. 3.8). The reagents are added to the two arms of the U tube; they diffuse slowly towards one another. In local regions where the concentration exceeds the solubility product, nuclei are formed and grow further into large crystals. Henisch and coworkers (1965) have made use of this method to grow crystals of calcium tartrate, calcium tungstate and lead iodide and have even incorporated selective impurity ions ( $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$  etc.) during growth.

Solids such as  $\text{KF}$ ,  $\text{PbO}$ ,  $\text{PbF}_2$  and  $\text{B}_2\text{O}_3$  are powerful solvents (flux) in the molten state for many inorganic substances and hence can be used as media for the growth of crystals. The usual technique is to dissolve the solute in a suitable combination of flux contained in a platinum crucible while maintaining the temperature slightly above the saturation point. After the crucible has been cooled at a programmed rate, the flux is poured off or leached away by mineral acid, leaving behind the crystals.

Figure 3.8. Gel method for growth of water-insoluble ionic solids.



Yttrium iron garnet and its isomorphs are typical examples of solids grown by the *flux method* using  $\text{PbO-PbF}_2$  fluxes. A recent development relating to growth of crystals from molten media is the use of molten metals as solvents from which crystals of intermetallic compounds are grown. Crystals of rare earth borides,  $\text{LnB}_4$  and  $\text{LnB}_6$ , have been grown from liquid aluminium and rare earth rhodium stannides from molten tin (Fisk *et al.*, 1972; Espinosa, 1980).

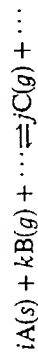
Electrolysis of molten salt solutions has been applied for preparation and crystal growth (Banks & Wold, 1974; Wold & Bellavance, 1972; Feigelson, 1980). The *electrolytic method* involves reduction, usually, of a cation and deposition of a product containing the reduced cation at the cathode. The technique was used by Andrieux and coworkers for the synthesis of a variety of transition metal compounds. Typical examples are: (i) growth of vanadium spinels,  $\text{MV}_2\text{O}_4$  ( $\text{M} = \text{Mn, Fe, Co, Zn}$  and  $\text{Mg}$ ), from  $\text{Na}_2\text{B}_4\text{O}_7$  and  $\text{NaF}$  melts using carbon crucibles and a carbon cathode (iron crucible and iron cathode for the iron compound), (ii) synthesis of  $\text{NaMO}_2$  ( $\text{M} = \text{Fe, Co, Ni}$ ) by the electrolysis of  $\text{NaOH}$  melts contained in alumina crucibles and  $\text{M}$  electrodes, (iii) synthesis of alkali metal tungsten bronzes,  $\text{A}_x\text{WO}_3$ , by the electrolysis of alkali metal tungstates using platinum electrodes. Although most of the early studies of fused-salt electrolysis were empirical, aimed at obtaining large single crystals by manipulating melt composition and current density, later studies as exemplified by the work of Whittingham and Huggins (1972) on the preparation of alkali metal tungsten bronze, have shown that if the potential difference across the cell rather than the current density is kept constant during electrolysis, crystals of fixed composition can be grown. The electrolysis method has been employed for the preparation and growth of crystals of a wide variety of solids such as borides, carbides, silicides, phosphides, arsenides, and sulphides.

The experimental cell assembly for electrolytic growth can be exceedingly simple or complex, depending on the system studied. For example, electrolytic growth of alkali metal tungsten bronzes requires a Gooch crucible set inside a bigger Gooch crucible, the inner crucible serving as the anode chamber and the outer one as the cathode chamber; electrodes of platinum or gold are used. No inert atmosphere is necessary since atmospheric oxygen has no influence upon the current-potential relationship. In contrast to this, the electrolytic cell used by Didchenko and Litz (1962) for the synthesis of  $\text{CeS}$  and  $\text{ThS}$  is quite elaborate, consisting of graphite and aluminium crucibles (serving as electrode compartments) together with molybdenum electrodes and involving a provision for inert atmosphere.

Growth of crystals from vapour may be divided into two categories

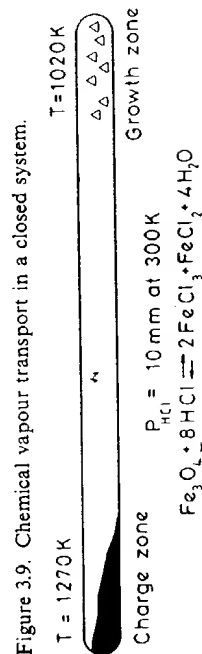


depending on whether the change, vapour  $\longrightarrow$  crystal, is physical or chemical. When the composition of the vapour and the crystal is the same, the process is physical; examples are sublimation-condensation and sputtering. The process is termed chemical when a chemical reaction occurs during the growth; in such a case, the composition of the solid is different from the vapour. The use of chemical vapour deposition (CVD) as a preparative technique was discussed earlier in this chapter (see Section 3.2.6). We shall now briefly discuss the related *chemical vapour transport* (CVT) which is useful both for preparation of new solids as well as growing them into crystals. The method has been treated extensively by Schäfer (1972) and Rosenberger (1981). In CVT, a condensed phase reacts with a gas to form volatile products. An equilibrium exists between the reactants and products:



CVT makes use of the temperature dependence of the above heterogeneous equilibrium to transport solid A through the vapour phase by means of gaseous intermediate(s) C. That the process involves true transport and not just evaporation and condensation is evident from the fact that solid A does not possess an appreciable vapour pressure at the experimental temperature; moreover, transport of A is not observed without the transporting agent B.

Chemical transport is normally carried out by maintaining a temperature difference between the charge end and growth end in a closed system (Fig. 3.9). The forward reaction occurs at the charge-end forming gaseous products and the reverse reaction occurs at the growth-end depositing crystals. The temperatures  $T_1$  and  $T_2$  chosen at the growth-end and charge-end respectively depend on whether the reaction is endothermic or exothermic. For endothermic reactions, transport requires that  $T_2 > T_1$ ; the reverse is true for exothermic reactions. The factors that determine growth of crystals by this method are, the choice of the chemical reaction chosen for transport (the CVT equilibrium should not lie at extremes lest the reversal becomes difficult), and the magnitude of  $T_1$  and  $T_2$  chosen and the concentration of transport agent used. The examples listed in Table 3.7 clearly suggest



that the method can be used to prepare or grow crystals of almost any type of solid material provided a suitable transporting agent that can give volatile products can be found. Metals have been transported using the volatile halides.

CVT is indeed a popular technique and has been employed to grow crystals of oxide phases such as  $\text{V}_8\text{O}_{15}$  free from contamination by the neighbouring Magnéli phases,  $\text{V}_7\text{O}_{13}$  and  $\text{V}_9\text{O}_{17}$ . The transporting agents commonly used are  $\text{I}_2$ ,  $\text{TeCl}_4$  and  $\text{Cl}_2$ . When a metal oxide can be volatilized readily (e.g.  $\text{SnO}_2 \xrightarrow{\text{heat}} \text{SnO} + \frac{1}{2}\text{O}_2$ ), the vapour species formed can be recombined to form single crystals at the cooler end.

*Molecular beam epitaxy* is an important technique for the preparation of semiconductors (III-V compounds). The finesse and sophistication of modern preparative solid state science is exemplified by this method which employs reactions of multiple molecular beams with a single crystal substrate.

When a polycrystalline solid sample is heated for a sufficient length of time below its melting point, an increase in the average size of crystals is observed. The driving force for this change is the lowering of outer crystalline area. The number of crystals obtained depends on the number of active nuclei capable of growing at the expense of the polycrystalline matrix. Metals are normally grown as crystals in the solid state by the so-called 'strain-anneal' procedure involving recrystallization by annealing out strain. Growth in the solid state is particularly useful for solids exhibiting incongruent melting or showing a polymorphic transition below the melting point.

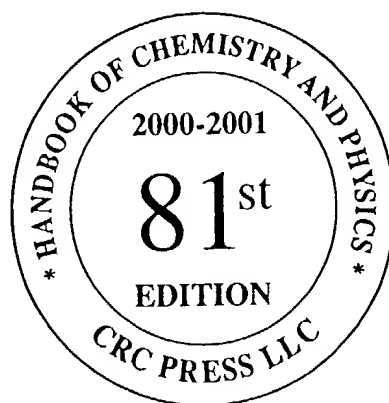
Table 3.7 Some crystals grown by chemical vapour transport method

Starting material	Final product (crystals)	Transport agent	Temperature, K
$\text{SiO}_2$	$\text{SiO}_2$	HF	470 $\longrightarrow$ 770
$\text{Fe}_3\text{O}_4$	$\text{Fe}_3\text{O}_4$	HCl	1270 $\longrightarrow$ 1070
$\text{Cr}_2\text{O}_3$	$\text{Cr}_2\text{O}_3$	$\text{Cl}_2 + \text{O}_2$	1070 $\longrightarrow$ 870
$\text{MO} + \text{Fe}_2\text{O}_3$ (M = Mg, Co, Ni)	$\text{MFe}_2\text{O}_4$	HCl	—
$\text{Nb} + \text{Nb}_2\text{O}_5$	NbO	$\text{Cl}_2$	—
$\text{NbSe}_2$	$\text{NbSe}_2$	$\text{I}_2$	1100 $\longrightarrow$ 1050

**ATTACHMENT C**

# CRC Handbook of Chemistry and Physics

A Ready-Reference Book of Chemical and Physical Data



Editor-in-Chief

David R. Lide, Ph.D.

Former Director, Standard Reference Data  
National Institute of Standards and Technology



CRC Press

Boca Raton London New York Washington, D.C.

# HIGH TEMPERATURE SUPERCONDUCTORS

## C. N. R. Rao and A. K. Raychaudhuri

The following tables give properties of a number of high temperature superconductors. Table 1 lists the crystal structure (space group and lattice constants) and the critical transition temperature  $T_c$  for the more important high temperature superconductors so far studied. Table 2 gives energy gap, critical current density, and penetration depth in the superconducting state. Table 3 gives electrical and thermal properties of some of these materials in the normal state. The tables were prepared in November 1992 and updated in November 1994.

### REFERENCES

1. Ginsburg, D.M., Ed., *Physical Properties of High-Temperature Superconductors*, Vols. I—III, World Scientific, Singapore, 1989—1992.
2. Rao, C.N.R., Ed., *Chemistry of High-Temperature Superconductors*, World Scientific, Singapore, 1991.
3. Shackelford, J.F., *The CRC Materials Science and Engineering Handbook*, CRC Press, Boca Raton, 1992, 98—99 and 122—123.
4. Kaldis, E., Ed., *Materials and Crystallographic Aspects of HT<sub>c</sub>-Superconductivity*, Kluwer Academic Publ., Dordrecht, The Netherlands, 1992.
5. Malik, S.K. and Shah, S.S., Ed., *Physical and Material Properties of High Temperature Superconductors*, Nova Science Publ., Commack, N.Y., 1994.
6. Chmaissem, O. et. al., *Physica*, C230, 231—238, 1994.
7. Antipov, E.V. et. al., *Physica*, C215, 1—10, 1993.

**Table 1**  
**Structural Parameters and Approximate  $T_c$  Values of High-Temperature Superconductors**

Material	Structure	$T_c$ /K (maximum value)
$\text{La}_2\text{CuO}_{4.8}$	Bmab; $a = 5.355$ , $b = 5.401$ , $c = 13.15$ Å	39
$\text{La}_{2-x}\text{Sr}_x(\text{Ba}_{1-x}\text{CuO}_4)$	I4/mmm; $a = 3.779$ , $c = 13.23$ Å	35
$\text{La}_2\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_2\text{O}_6$	I4/mmm; $a = 3.825$ , $c = 19.42$ Å	60
$\text{YBa}_2\text{Cu}_3\text{O}_7$	Pmmm; $a = 3.821$ , $b = 3.885$ , $c = 11.676$ Å	93
$\text{YBa}_2\text{Cu}_4\text{O}_8$	Ammm; $a = 3.84$ , $b = 3.87$ , $c = 27.24$ Å	80
$\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$	Ammm; $a = 3.851$ , $b = 3.869$ , $c = 50.29$ Å	93
$\text{Bi}_2\text{Sr}_2\text{CuO}_6$	Amaa; $a = 5.362$ , $b = 5.374$ , $c = 24.622$ Å	10
$\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$	$A_2aa$ ; $a = 5.409$ , $b = 5.420$ , $c = 30.93$ Å	92
$\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}$	$A_2aa$ ; $a = 5.39$ , $b = 5.40$ , $c = 37$ Å	110
$\text{Bi}_2\text{Sr}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_{10}$	P4/mmm; $a = 3.888$ , $c = 17.28$ Å	25
$\text{Ti}_2\text{Ba}_2\text{CuO}_6$	$A_2aa$ ; $a = 5.468$ , $b = 5.472$ , $c = 23.238$ Å;	
	I4/mmm; $a = 3.866$ , $c = 23.239$ Å	92
$\text{Ti}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$	I4/mmm; $a = 3.855$ , $c = 29.318$ Å	119
$\text{Ti}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$	I4/mmm; $a = 3.85$ , $c = 35.9$ Å	128
$\text{Ti}(\text{BaLa})\text{CuO}_5$	P4/mmm; $a = 3.83$ , $c = 9.55$ Å	40
$\text{Ti}(\text{SrLa})\text{CuO}_5$	P4/mmm; $a = 3.7$ , $c = 9$ Å	40
$(\text{Ti}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{CuO}_5$	P4/mmm; $a = 3.738$ , $c = 9.01$ Å	40
$\text{TiCaBa}_2\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.856$ , $c = 12.754$ Å	103
$(\text{Ti}_{0.5}\text{Pb}_{0.5})\text{CaSr}_2\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.80$ , $c = 12.05$ Å	90
$\text{TiSr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.80$ , $c = 12.10$ Å	90
$\text{TiCa}_2\text{Ba}_2\text{Cu}_3\text{O}_8$	P4/mmm; $a = 3.853$ , $c = 15.913$ Å	110
$(\text{Ti}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$	P4/mmm; $a = 3.81$ , $c = 15.23$ Å	120
$\text{TiBa}_2(\text{La}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_9$	I4/mmm; $a = 3.8$ , $c = 29.5$ Å	40
$\text{Pb}_2\text{Sr}_2\text{La}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_8$	Cmmm; $a = 5.435$ , $b = 5.463$ , $c = 15.817$ Å	70
$\text{Pb}_2(\text{SrLa})_2\text{Cu}_2\text{O}_6$	P22 <sub>1</sub> 2; $a = 5.333$ , $b = 5.421$ , $c = 12.609$ Å	32
$(\text{Pb,Cu})\text{Sr}_2(\text{La,Ca})\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.820$ , $c = 11.826$ Å	50
$(\text{Pb,Cu})(\text{Sr,Eu})(\text{Eu,Ce})\text{Cu}_2\text{O}_x$	I4/mmm; $a = 3.837$ , $c = 29.01$ Å	25
$\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$	I4/mmm; $a = 3.95$ , $c = 12.07$ Å	30
$\text{Ca}_{1-x}\text{Sr}_x\text{CuO}_2$	P4/mmm; $a = 3.902$ , $c = 3.35$ Å	110
$\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$	P4/mmm; $a = 3.942$ , $c = 3.393$ Å	40
$\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$	Pm3m; $a = 4.287$ Å	31
$\text{Rb}_2\text{CsC}_{60}$	$a = 14.493$ Å	31
$\text{NdBa}_2\text{Cu}_3\text{O}_7$	Pmmm; $a = 3.878$ , $b = 3.913$ , $c = 11.753$	58

# HIGH TEMPERATURE SUPERCONDUCTORS (continued)

**Table 1**  
Structural Parameters and Approximate  $T_c$  Values of High-Temperature Superconductors  
(continued)

Material	Structure	$T_c$ /K (maximum value)
SmBaSrCu <sub>3</sub> O <sub>7</sub>	I4/mmm; $a = 3.854, c = 11.62$	84
EuBaSrCu <sub>3</sub> O <sub>7</sub>	I4/mmm; $a = 3.845, c = 11.59$	88
GdBaSrCu <sub>3</sub> O <sub>7</sub>	I4/mmm; $a = 3.849, c = 11.53$	86
DyBaSrCu <sub>3</sub> O <sub>7</sub>	Pmmm; $a = 3.802, b = 3.850, c = 11.56$	90
HoBaSrCu <sub>3</sub> O <sub>7</sub>	Pmmm; $a = 3.794, b = 3.849, c = 11.55$	87
ErBaSrCu <sub>3</sub> O <sub>7</sub> (multiphase)	Pmmm; $a = 3.787, b = 3.846, c = 11.54$	82
TmBaSrCu <sub>3</sub> O <sub>7</sub> (multiphase)	Pmmm; $a = 3.784, b = 3.849, c = 11.55$	88
YBaSrCu <sub>3</sub> O <sub>7</sub>	Pmmm; $a = 3.803, b = 3.842, c = 11.54$	84
HgBa <sub>2</sub> CuO <sub>4</sub>	I4/mmm; $a = 3.878, c = 9.507$	94
HgBa <sub>2</sub> CaCu <sub>2</sub> O <sub>6</sub> (annealed in O <sub>2</sub> )	I4/mmm; $a = 3.862, c = 12.705$	127
HgBa <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>8</sub>	Pmmm; $a = 3.85, c = 15.85$	133
HgBa <sub>2</sub> Ca <sub>3</sub> Cu <sub>4</sub> O <sub>10</sub>	Pmmm; $a = 3.854, c = 19.008$	126

**Table 2**  
Superconducting Properties

$J_c(0)$ : Critical current density extrapolated to 0 K

$\lambda_{ab}$ : Penetration depth in  $a$ - $b$  plane

$k_B$ : Boltzmann constant

Material	Form	Energy gap ( $\Delta$ )		$10^{-6} \times J_c(0)/A \text{ cm}^{-2}$	$\lambda_{ab}/\text{\AA}$
		$2\Delta_{pp}/k_B T_c^*$	$2\Delta_{fit}/k_B T_c^\dagger$		
Y Ba <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	Single Crystal	5-6	4-5	30 (film)	1400
Bi <sub>2</sub> Sr <sub>2</sub> CaCu <sub>2</sub> O <sub>8</sub>	Single Crystal	8-9	5.5-6.5	2	2700
Tl <sub>2</sub> Ba <sub>3</sub> CaCu <sub>2</sub> O <sub>8</sub>	Ceramic	6-7	4-6	10 (film, 80 K)	2000
La <sub>2-x</sub> Sr <sub>x</sub> CuO <sub>4</sub> , $x = 0.15$	Ceramic	7-9	4-6		
Nd <sub>2-x</sub> Ce <sub>x</sub> CuO <sub>4</sub>	Ceramic	8	4-5	0.2 (film)	

\* Obtained from peak to peak value.

† Obtained from fit to BCS-type relation.

**ATTACHMENT D**

# HIGH TEMPERATURE SUPERCONDUCTORS

C. N. R. Rao and A. K. Raychaudhuri

The following tables give properties of a number of high temperature superconductors. Table 1 lists the crystal structure (space group and lattice constants) and the critical transition temperature  $T_c$  for the more important high temperature superconductors so far studied. Table 2 gives energy gap, critical current density, and penetration depth in the superconducting state. Table 3 gives electrical and thermal properties of some of these materials in the normal state. The tables were prepared in November 1992 and updated in November 1994.

## REFERENCES

1. Ginsburg, D.M., Ed., *Physical Properties of High-Temperature Superconductors*, Vols. I—III, World Scientific, Singapore, 1989—1992.
2. Rao, C.N.R., Ed., *Chemistry of High-Temperature Superconductors*, World Scientific, Singapore, 1991.
3. Shackelford, J.F., *The CRC Materials Science and Engineering Handbook*, CRC Press, Boca Raton, 1992, 98—99 and 122—123.
4. Kaldis, E., Ed., *Materials and Crystallographic Aspects of HT<sub>c</sub>-Superconductivity*, Kluwer Academic Publ., Dordrecht, The Netherlands, 1992.
5. Malik, S.K. and Shah, S.S., Ed., *Physical and Material Properties of High Temperature Superconductors*, Nova Science Publ., Commack, N.Y., 1994.
6. Chmaissem, O. et. al., *Physica*, C230, 231—238, 1994.
7. Antipov, E.V. et. al., *Physica*, C215, 1—10, 1993.

**Table 1**  
**Structural Parameters and Approximate  $T_c$  Values of High-Temperature Superconductors**

Material	Structure	$T_c$ /K (maximum value)
* 1 $\text{La}_2\text{CuO}_{4.6}$	Bmab; $a = 5.355$ , $b = 5.401$ , $c = 13.15$ Å	39
2 $\text{La}_{2-x}\text{Sr}_x(\text{Ba}_y)\text{CuO}_4$	I4/mmm; $a = 3.779$ , $c = 13.23$ Å	35
3 $\text{La}_2\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_2\text{O}_6$	I4/mmm; $a = 3.825$ , $c = 19.42$ Å	60
4 $\text{YBa}_2\text{Cu}_3\text{O}_7$	Pmmm; $a = 3.821$ , $b = 3.885$ , $c = 11.676$ Å	93
5 $\text{YBa}_2\text{Cu}_4\text{O}_8$	Ammm; $a = 3.84$ , $b = 3.87$ , $c = 27.24$ Å	80
6 $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$	Ammm; $a = 3.851$ , $b = 3.869$ , $c = 50.29$ Å	93
* 7 $\text{Bi}_2\text{Sr}_2\text{CuO}_6$	Amaa; $a = 5.362$ , $b = 5.374$ , $c = 24.622$ Å	10
* 8 $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$	A <sub>2</sub> aa; $a = 5.409$ , $b = 5.420$ , $c = 30.93$ Å	92
* 9 $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}$	A <sub>2</sub> aa; $a = 5.39$ , $b = 5.40$ , $c = 37$ Å	110
* 10 $\text{Bi}_2\text{Sr}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_{10}$	P4/mmm; $a = 3.888$ , $c = 17.28$ Å	25
* 11 $\text{Ti}_2\text{Ba}_2\text{CuO}_6$	A <sub>2</sub> aa; $a = 5.468$ , $b = 5.472$ , $c = 23.238$ Å; I4/mmm; $a = 3.866$ , $c = 23.239$ Å	92
* 12 $\text{Ti}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$	I4/mmm; $a = 3.855$ , $c = 29.318$ Å	119
* 13 $\text{Ti}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$	I4/mmm; $a = 3.85$ , $c = 35.9$ Å	128
14 $\text{Ti}(\text{BaLa})\text{CuO}_5$	P4/mmm; $a = 3.83$ , $c = 9.55$ Å	40
15 $\text{Ti}(\text{SrLa})\text{CuO}_5$	P4/mmm; $a = 3.7$ , $c = 9$ Å	40
* 16 $(\text{Ti}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{CuO}_5$	P4/mmm; $a = 3.738$ , $c = 9.01$ Å	40
* 17 $\text{TiCaBa}_2\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.856$ , $c = 12.754$ Å	103
* 18 $(\text{Ti}_{0.5}\text{Pb}_{0.5})\text{CaSr}_2\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.80$ , $c = 12.05$ Å	90
19 $\text{TiSr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.80$ , $c = 12.10$ Å	90
* 20 $\text{TiCa}_2\text{Ba}_2\text{Cu}_3\text{O}_8$	P4/mmm; $a = 3.853$ , $c = 15.913$ Å	110
* 21 $(\text{Ti}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$	P4/mmm; $a = 3.81$ , $c = 15.23$ Å	120
22 $\text{TiBa}_2(\text{La}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_9$	I4/mmm; $a = 3.8$ , $c = 29.5$ Å	40
23 $\text{Pb}_2\text{Sr}_2\text{La}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_8$	Cmmm; $a = 5.435$ , $b = 5.463$ , $c = 15.817$ Å	70
24 $\text{Pb}_2(\text{SrLa})_2\text{Cu}_2\text{O}_6$	P22 <sub>1</sub> 2; $a = 5.333$ , $b = 5.421$ , $c = 12.609$ Å	32
25 $(\text{Pb,Cu})\text{Sr}_2(\text{La,Ca})\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.820$ , $c = 11.826$ Å	50
26 $(\text{Pb,Cu})(\text{Sr,Eu})(\text{Eu,Ce})\text{Cu}_2\text{O}_x$	I4/mmm; $a = 3.837$ , $c = 29.01$ Å	25
* 27 $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$	I4/mmm; $a = 3.95$ , $c = 12.07$ Å	30
* 28 $\text{Ca}_{1-x}\text{Sr}_x\text{CuO}_2$	P4/mmm; $a = 3.902$ , $c = 3.35$ Å	110
29 $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$	P4/mmm; $a = 3.942$ , $c = 3.393$ Å	40
* 30 $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$	Pm3m; $a = 4.287$ Å	31
* 31 $\text{Rb}_2\text{CsC}_{60}$	$a = 14.493$ Å	31
32 $\text{NdBa}_2\text{Cu}_3\text{O}_7$	Pmmm; $a = 3.878$ , $b = 3.913$ , $c = 11.753$	58

# HIGH TEMPERATURE SUPERCONDUCTORS (continued)

**Table 1**  
Structural Parameters and Approximate  $T_c$  Values of High-Temperature Superconductors  
(continued)

Material	Structure	$T_c$ /K (maximum value)
33 SmBaSrCu <sub>3</sub> O <sub>7</sub>	I4/mmm; $a = 3.854$ , $c = 11.62$	84
34 EuBaSrCu <sub>3</sub> O <sub>7</sub>	I4/mmm; $a = 3.845$ , $c = 11.59$	88
35 GdBaSrCu <sub>3</sub> O <sub>7</sub>	I4/mmm; $a = 3.849$ , $c = 11.53$	86
36 DyBaSrCu <sub>3</sub> O <sub>7</sub>	Pmmm; $a = 3.802$ , $b = 3.850$ , $c = 11.56$	90
37 HoBaSrCu <sub>3</sub> O <sub>7</sub>	Pmmm; $a = 3.794$ , $b = 3.849$ , $c = 11.55$	87
38 ErBaSrCu <sub>3</sub> O <sub>7</sub> (multiphase)	Pmmm; $a = 3.787$ , $b = 3.846$ , $c = 11.54$	82
39 TmBaSrCu <sub>3</sub> O <sub>7</sub> (multiphase)	Pmmm; $a = 3.784$ , $b = 3.849$ , $c = 11.55$	88
40 YBaSrCu <sub>3</sub> O <sub>7</sub>	Pmmm; $a = 3.803$ , $b = 3.842$ , $c = 11.54$	84
* 41 HgBa <sub>2</sub> CuO <sub>4</sub>	I4/mmm; $a = 3.878$ , $c = 9.507$	94
* 42 HgBa <sub>2</sub> CaCu <sub>2</sub> O <sub>6</sub> (annealed in O <sub>2</sub> )	I4/mmm; $a = 3.862$ , $c = 12.705$	127
* 43 HgBa <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>8</sub>	Pmmm; $a = 3.85$ , $c = 15.85$	133
* 44 HgBa <sub>2</sub> Ca <sub>3</sub> Cu <sub>4</sub> O <sub>10</sub>	Pmmm; $a = 3.854$ , $c = 19.008$	126

**Table 2**  
Superconducting Properties

$J_c(0)$ : Critical current density extrapolated to 0 K  
 $\lambda_{ab}$ : Penetration depth in  $a$ - $b$  plane  
 $k_B$ : Boltzmann constant

Material	Form	Energy gap ( $\Delta$ )		$10^{-6} \times J_c(0)/A \text{ cm}^{-2}$	$\lambda_{ab}/\text{\AA}$
		$2\Delta_{pp}/k_B T_c^*$	$2\Delta_{fl}/k_B T_c^\dagger$		
Y Ba <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	Single Crystal	5-6	4-5	30 (film)	1400
Bi <sub>2</sub> Sr <sub>2</sub> CaCu <sub>2</sub> O <sub>8</sub>	Single Crystal	8-9	5.5-6.5	2	2700
Tl <sub>2</sub> Ba <sub>3</sub> CaCu <sub>2</sub> O <sub>8</sub>	Ceramic	6-7	4-6	10 (film, 80 K)	2000
La <sub>2-x</sub> Sr <sub>x</sub> CuO <sub>4</sub> , $x = 0.15$	Ceramic	7-9	4-6		
Nd <sub>2-x</sub> Ce <sub>x</sub> CuO <sub>4</sub>	Ceramic	8	4-5	0.2 (film)	

\* Obtained from peak to peak value.  
† Obtained from fit to BCS-type relation.



**ATTACHMENT E**

ERCONDUCTIVITY

Temperature

Temperature

Temperature

Superconductivity

Physics

conductors

erconductivity

ma)

shop on Towards the  
uctors

ty

pics — 1st Asia-Pacific

Superconductivity

Temperature

Superconductivity

# PHYSICAL PROPERTIES OF HIGH TEMPERATURE SUPERCONDUCTORS I

Editor

**Donald M. Ginsberg**

*Professor of Physics*

*University of Illinois at Urbana-Champaign*



**World Scientific**

Singapore • New Jersey • London • Hong Kong

*Published by*

**World Scientific Publishing Co. Pte. Ltd.**  
P O Box 128, Farrer Road, Singapore 9128

*USA office:* World Scientific Publishing Co., Inc.  
687 Hartwell Street, Teaneck, NJ 07666, USA

*UK office:* World Scientific Publishing Co. Pte. Ltd.  
73 Lynton Mead, Totteridge, London N20 8DH, England

**PHYSICAL PROPERTIES OF HIGH TEMPERATURE SUPERCONDUCTORS I**

Copyright © 1989 by World Scientific Publishing Co. Pte. Ltd.

*All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the Publisher.*

ISBN 9971-50-683-1  
9971-50-894-X (pbk)

Printed in Singapore by Utopia Press.

537.623

Physic

1989

*This book is de  
rised to the hig*

513

## CONTENTS

Preface	vii
Chapter 1: Introduction, History, and Overview of High Temperature Superconductivity <i>D.M. Ginsberg</i>	1
Chapter 2: Thermodynamic Properties, Fluctuations, and Anisotropy of High Temperature Superconductors <i>M.B. Salamon</i>	39
Chapter 3: Macroscopic Magnetic Properties of High Temperature Superconductors <i>A.P. Malozemoff</i>	71
Chapter 4: Neutron Scattering Studies of Structural and Magnetic Excitations in Lamellar Copper Oxides — A Review <i>R.J. Birgeneau and G. Shirane</i>	151
Chapter 5: Normal State Transport and Elastic Properties of High $T_c$ Materials and Related Compounds <i>P.B. Allen, Z. Fisk, and A. Migliori</i>	213
Chapter 6: Rare Earth and Other Substitutions in High Temperature Oxide Superconductors <i>J.T. Markert, Y. Dalichaouch, and M.B. Maple</i>	265
Chapter 7: Infrared Properties of High $T_c$ Superconductors <i>T. Timusk and D.B. Tanner</i>	339
Chapter 8: Raman Scattering in High- $T_c$ Superconductors <i>C. Thomsen and M. Cardona</i>	409
Subject Index	509

# PHYSICAL PROPERTIES OF HIGH TEMPERATURE SUPERCONDUCTORS II

Editor

**Donald M. Ginsberg**

*Department of Physics*

*University of Illinois at Urbana — Champaign*

 **World Scientific**  
*Singapore • New Jersey • London • Hong Kong*

*Published by*

World Scientific Publishing Co. Pte. Ltd.

P O Box 128, Farrer Road, Singapore 9128

USA office: 687 Hartwell Street, Teaneck, NJ 07666

UK office: 73 Lynton Mead, Totteridge, London N20 8DH

*This  
John*

**PHYSICAL PROPERTIES OF HIGH TEMPERATURE  
SUPERCONDUCTORS II**

Copyright © 1990 by World Scientific Publishing Co. Pte. Ltd.

*All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the Publisher.*

ISBN 981-02-0124-9

981-02-0190-7 (pbk)

Printed in Singapore by JBW Printers & Binders Pte. Ltd.

## CONTENTS

Preface	vii
Chapter 1. Introduction: A Description of Some New Materials and An Overview of This Book <i>D.M. Ginsberg</i>	1
Chapter 2. Specific Heat of High Temperature Superconductors: A Review <i>A. Junod</i>	13
Chapter 3. Crystal Structures of High-Temperature Superconductors <i>R.M. Hazen</i>	121
Chapter 4. The Microstructure of High-Temperature Oxide Superconductors <i>C.H. Chen</i>	199
Chapter 5. Nuclear Resonance Studies of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ <i>C.H. Pennington and C.P. Slichter</i>	269
Chapter 6. Electronic Structure, Surface Properties, and Interface Chemistry of High Temperature Superconductors <i>H.M. Meyer III and J. H. Weaver</i>	369
Chapter 7. The Hall Effect and its Relation to other Transport Phenomena in the Normal State of the High-Temperature Superconductors <i>N.P. Ong</i>	459
Chapter 8. Oxygen Stoichiometric Effects and Related Atomic Substitutions in the High- $T_c$ Cuprates <i>L.H. Greene and B.G. Bagley</i>	509
Chapter 9. The Pairing State of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ <i>J.F. Annett, N. Goldenfeld and S.R. Renn</i>	571
Subject Index	687
Appendix A	697
Appendix B	699

**ATTACHMENT F**



# CHEMISTRY OF HIGH TEMPERATURE SUPERCONDUCTORS

Edited by

**C. N. R. RAO, F. R. S.**

*CSIR Centre of Excellence in Chemistry and  
Solid State and Structural Chemistry Unit  
Indian Institute of Science, Bangalore, India*



**World Scientific**

*Singapore • New Jersey • London • Hong Kong*

Published by

World Scientific Publishing Co. Pte. Ltd.

P O Box 128, Farrer Road, Singapore 9128

USA office: Suite 1B, 1060 Main Street, River Edge, NJ 07661

UK office: 73 Lynton Mead, Totteridge, London N20 8DH

### Library of Congress Cataloging-in-Publication Data

Chemistry of high-temperature: superconductors/edited by C.N.R. Rao.

P. cm.

Includes bibliographical references.

ISBN 9810208057

1. High temperature superconductors. 2. Superconductivity-Chemistry. 3. Solid state chemistry. I. Rao, C. N. R.

(Chinnamoni Nagasa Ramachandra), 1934-

QC611.98.H54C47 1991

527.623-dc20

91-32649

CIP

Copyright © 1991 by World Scientific Publishing Co. Pte. Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the Publisher.

Printed in Singapore by Utopia Press.

Library

University of Miami

## PREFACE

Superconductivity has become one of the most active areas of research in physical sciences in the last few years, because of the advent of high-temperature superconductivity in oxide materials, especially the cuprates. Since the initial discovery of 30 K superconductivity in the La-Ba system by Bednorz and Müller, a variety of materials with novel structural features have been synthesized and characterized. Several interesting correlations between the structure and the properties of superconducting materials have been unravelled. While most cuprate superconductors have holes as charge carriers, electron superconducting cuprates have been discovered. There are also a few oxide superconductors which do not contain copper in them. In all these developments, chemists have made important contributions. In this volume an effort has been made to present the status of the chemistry of high-temperature oxide superconductors. It is possible that certain aspects such as crystal growth and measurement of single crystals have not been adequately covered in this volume. However, the various articles presented here should cover most of the salient features of high-temperature oxide superconductors with respect to their structure, properties, and preparation. Wherever possible preparative aspects are highlighted and two review articles deal with thin films besides one article on tapes. I believe that by going through the articles in this volume, or by consulting the references, one can get a nearly complete picture of the present status of high-temperature oxide superconductors, with a useful reference to most of the recent literature. It is hoped that some of the topics mentioned in these articles would also stimulate further research.

High-temperature superconductivity itself is going through a rapid phase today. Newer materials are likely to be discovered in the near future. We already have the alkali metal doped buckminsterfullerene,  $C_{60}$ , with superconductivity around 40 K.

I do hope that the present volume will be found useful by students, teachers, and practitioners.

C.N.R.

Ban

Juli

## CONTENTS

Preface . . . . .	v
Crystal Chemistry and Superconductivity in the Copper Oxides . . . . . <i>J. B. Goodenough and A. Manthiram</i>	1
Defects and Microstructures in Layered Copper Oxides . . . . . <i>M. Hervieu, B. Domengès, C. Michel, and B. Raveau</i>	57
Important Common Features of the Cuprate Superconductors: Relation Between the Electronic Structure and Superconductivity . . . . . <i>C. N. R. Rao</i>	87
Design of New Cuprate Superconductors and Prediction of Their Structures . . . . . <i>Takahisa Arima and Yoshinori Tokura</i>	104
Structure and Superconductivity in Y-123 and Related Compounds . . . . . <i>G. V. Subba Rao and U. V. Varadaraju</i>	126
Chemistry of Superconducting Bismuth, Thallium and Lead Cuprates . . . . . <i>J. Gopalakrishnan</i>	156
The Modulation in Bismuth Cuprates and Related Materials . . . . . <i>J. W. Tarascon, W. R. McKinnon, and Y. LePage</i>	186
Electron-Doped High $T_c$ Cuprate Superconductors . . . . . <i>Carmen C. Almasan and M. Brian Maple</i>	205
Application of High-Pressure and High Oxygen Pressure to Cu-Oxides . . . . . <i>M. Takano, Z. Hiroi, M. Azuma, and Y. Takeda</i>	243
Copper-Less Oxide Superconductors . . . . . <i>A. M. Umarji</i>	267
Synthesis, Structure and Properties of $\text{La}_2\text{NiO}_{4+\delta}$ . . . . . <i>Douglas J. Buttrey and Jurgen M. Honig</i>	283

Thermodynamics of Y-Ba-Cu-O System and Related Aspects . . . . .	306
<i>S. F. Pashin and Yu. D. Tretyakov</i>	
Investigation of the Electronic Structure of the Cuprate Superconductors Using High-Energy Spectroscopies . . . . .	348
<i>D. D. Sarma</i>	
Field Modulated Microwave Absorption in High-Temperature Superconducting Oxides . . . . .	379
<i>Micky Puri and Larry Kevan</i>	
Grain Alignment and its Effect on Critical Current Properties of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x/\text{Ag}$ Superconducting Tape . . . . .	399
<i>K. Togano, H. Kumakura, H. Maeda, and J. Kase</i>	
High $T_c$ Superconducting Thin Films - Processing Methods and Properties . . . . .	411
<i>S. Mohan</i>	
High Temperature Superconductor Thin Films by Pulsed Laser Ablation . . . . .	454
<i>S. B. Ogale</i>	
Magnetic Properties and Field Modulated Microwave Absorption of $\text{YBa}_2\text{Cu}_3\text{O}_7$ Thin Films . . . . .	484
<i>C. Schlenker, J. Dumas, C. L. Liu, and S. Revenaz</i>	

Published by

World Scientific Publishing Co. Pte. Ltd.

P O Box 128, Farrer Road, Singapore 9128

USA office: Suite 1B, 1060 Main Street, River Edge, NJ 07661

UK office: 73 Lynton Mead, Totteridge, London N20 8DH

Library of Congress Cataloging-in-Publication Data

Chemistry of high-temperature: superconductors/edited by C.N.R.  
Rao.

p. cm.

Includes bibliographical references.

ISBN 9810208057

1. High temperature superconductors. 2. Superconductivity-  
Chemistry. 3. Solid state chemistry. I. Rao, C. N. R.  
(Chintamani Nagesa Ramachandra), 1934-

QC611.98.H54C47 1991

527.623--dc20

91-32649

CIP

Copyright © 1991 by World Scientific Publishing Co. Pte. Ltd.

*All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the Publisher.*

Printed in Singapore by Utopia Press.

Library

University of Miami

Sub  
in ph  
temp  
Since  
system  
featu  
tions  
mater  
holes  
disco  
copp  
impor  
the s  
is pos  
single  
the v  
high-  
struct  
lighte  
tapes  
be ab  
mical  
refere  
menti  
Hig  
phase  
We al  
super  
Id  
and p

**ATTACHMENT G**

# **The CRC Materials Science and Engineering Handbook**

Editor

**James F. Shackelford**

Professor of Materials Science and Engineering

Division of Materials Science and Engineering

and

Associate Dean of the College of Engineering

University of California, Davis

Associate Editor

**William Alexander**

Research Engineer

Division of Materials Science and Engineering

University of California, Davis



**CRC Press**

**Boca Raton Ann Arbor London**

Library of Congress Cataloging-in-Publication Data

Catalog record is available from the Library of Congress

ISBN 0-8493-4276-7

This book represents information obtained from authentic and highly regarded sources. Reprinted material is quoted with permission, and sources are indicated. A wide variety of references are listed. Every reasonable effort has been made to give reliable data and information, but the author and the publisher cannot assume responsibility for the validity of all materials or for the consequences of their use.

All rights reserved. This book, or any parts thereof, may not be reproduced in any form without written consent from the publisher.

Direct all inquiries to CRC Press, Inc., 2000 Corporate Blvd., N. W., Boca Raton, Florida, 33431.

© 1992 by CRC Press, Inc.

International Standard Book Number 0-8493-4276-7

Printed in the United States 0 1 2 3 4 5 6 7 8 9

Th

Eng

Bon



## TABLE OF CONTENTS

The Elements .....	1
Elements for Engineering Materials .....	2
Elements in the Earth's Crust .....	4
The Periodic Table of The Elements .....	6
The Metallic Elements .....	7
The Elements in Ceramic Materials .....	8
The Elements in Polymeric Materials .....	9
The Elements in Semiconducting Materials .....	10
Available Stable Isotopes of the Elements .....	12
Properties of Selected Elements .....	20
Melting Points of Selected Elements .....	26
Densities of Selected Elements .....	28
Crystal Structure of the Elements .....	30
Atomic and Ionic Radii of the Elements .....	34
Atomic Radii of the Elements .....	39
Ionic Radii of the Elements .....	41
Selected Properties of Superconductive Elements .....	43
$T_c$ for Thin Films of Superconductive Elements .....	44
Engineering Compounds .....	47
Engineering Ceramics .....	48
Refractories, Ceramics, and Salts .....	53
Type II Superconducting Compounds:	
Critical Temperature and Crystal Structure Data .....	65
High Temperature Superconducting Compounds:	
Critical Temperature and Crystal Structure Data .....	98
Crystal Structure Types .....	101
Critical Temperature Data for	
Type II Superconducting Compounds .....	104
Selected Superconductive Compounds And Alloys:	
Critical Field Data .....	121
$T_c$ Data for High Temperature Superconducting Compounds .....	122
Bonding, Thermodynamic, and Kinetic Data .....	125
Bond Strengths in Diatomic Molecules	
(Listed by Molecule) .....	126
(Listed by Bond Strength) .....	135
Bond Strengths of Polyatomic Molecules	
(Listed by Molecule) .....	144
(Listed by Bond Strength) .....	147

## Table of Contents (Continued)

Carbon Bond Lengths (Periodic Table Presentation) .....	150
Carbon Bond Lengths .....	151
Bond Length Values Between Elements	
(Listed by Bond) .....	154
(Listed by Bond Length) .....	156
Bond Angle Values Between Elements	
(Listed by Bond) .....	158
(Listed by Bond Angle) .....	159
Heat of Formation of Selected Inorganic Oxides .....	160
Heats of Sublimation (at 25°C) of Selected Metals	
and their Oxides .....	173
Melting Points of Selected Elements and Inorganic Compounds	
(Listed by Element or Compound) .....	174
(Listed by Melting Point) .....	186
Melting Points of Ceramics	
(Listed by Compound) .....	198
(Listed by Melting Point) .....	202
Heat of Fusion For Selected Elements and	
Inorganic Compounds .....	206
Surface Tension of Liquid Elements .....	218
Vapor Pressure of the Elements	
(Very Low Pressures) .....	235
(Moderate Pressures) .....	237
(High Pressures) .....	240
Specific Heat of Selected Elements at 25 °C	
(Listed by Element) .....	243
(Listed by Specific Heat) .....	248
Heat Capacity of Selected Ceramics .....	253
Specific Heat of Selected Polymers .....	255
Phase Change Thermodynamic Properties	
for Selected Elements .....	260
for Selected Oxides .....	269
Thermodynamic Coefficients	
Description .....	281
for Selected Elements .....	283
for Selected Oxides .....	292
Thermal Conductivity of Metals	
at Cryogenic Temperatures .....	305
at 100 to 3000 K .....	321

## Table of Contents (Continued)

Thermal Conductivity of Selected Ceramics .....	334
Thermal Conductivity of Special Concretes .....	345
Thermal Conductivity of Cryogenic Insulation and Supports .....	346
Thermal Conductivity of Selected Polymers .....	348
Thermal Expansion of Selected Tool Steels .....	355
Thermal Expansion and Thermal Conductivity of Selected Alloy Cast Irons .....	356
Thermal Expansion of Selected Ceramics .....	357
Thermal Expansion Coefficients for Materials used in Integrated Circuits .....	374
Thermal Expansion of Selected Polymers .....	376
Values of The Error Function .....	384
Diffusion in Selected Metallic Systems .....	385
Diffusivity Values of Metals into Metals .....	406
Diffusion in some Non-Metallic Systems .....	416
Diffusion in Semiconductors .....	417
Temper Designation System for Aluminum Alloys .....	424
Structure, Compositions, and Phase Diagram Sources .....	425
The Seven Crystal Systems .....	426
The Fourteen Bravais Lattices .....	427
Structure of Selected Ceramics .....	428
Density of Selected Tool Steels .....	434
Density of Selected Alloy Cast Irons .....	435
Density of Selected Ceramics .....	436
Specific Gravity of Selected Polymers .....	439
Composition Limits of Selected Tool Steels .....	450
Composition Limits of Selected Gray Cast Irons .....	459
Composition Limits of Selected Ductile Irons .....	464
Composition Ranges for Selected Malleable Irons .....	468
Composition Ranges for Selected Carbon Steels .....	470
Composition Ranges for Selected Resulfurized Carbon Steels .....	475
Composition Ranges for Selected Alloy Steels .....	478
Composition Ranges for Selected Cast Aluminum Alloys .....	498
Composition Ranges for Selected Wrought Aluminum Alloys .....	502
Typical Composition of Selected Glass-Ceramics .....	506
Phase Diagram Sources .....	510

## Table of Contents (Continued)

Mechanical Properties .....	511
Mechanical Properties of Selected Tool Steels .....	512
Tool Steel Softening After 100 Hours for Various Temperatures .....	518
Mechanical Properties of Selected Gray Cast Irons .....	519
Mechanical Properties of Selected Ductile Irons .....	521
Average Mechanical Properties of Treated Ductile Irons .....	523
Mechanical Properties of Selected Malleable Iron Castings .....	525
Young's Modulus of Selected Ceramics .....	528
Modulus of Elasticity in Tension for Selected Polymers .....	534
Poisson's Ratio for Selected Ceramics .....	538
Yield Strength of Selected Cast Aluminum Alloys (Listed by Alloy) .....	541
(Listed by Yield Strength ) .....	544
Yield Strength of Selected Wrought Aluminum Alloys (Listed by Alloy) .....	547
(Listed by Yield Strength ) .....	555
Yield Strength of Selected Polymers .....	563
Tensile Strength of Selected Aluminum Casting Alloys (Listed by Alloy) .....	567
(Listed by Tensile Strength ) .....	570
Tensile Strength of Selected Wrought Aluminum Alloys (Listed by Alloy) .....	573
(Listed by Tensile Strength ) .....	581
Tensile Strength of Selected Ceramics .....	589
Tensile Strength of Selected Polymers .....	593
Total Elongation of Selected Cast Aluminum Alloys (Listed by Alloy) .....	601
(Listed by Total Elongation ) .....	604
Total Elongation of Selected Polymers .....	607
Elongation at Yield of Selected Polymers .....	615
Shear Strength of Selected Wrought Aluminum Alloys (Listed by Alloy) .....	617
(Listed by Shear Strength) .....	624
Hardness of Selected Wrought Aluminum Alloys (Listed by Alloy) .....	631
(Listed by Hardness) .....	636
Hardness of Selected Ceramics .....	641
Hardness of Selected Polymers .....	647

EI

CI

## Table of Contents (Continued)

Impact Strength of Selected Polymers .....	657
Compressive Yield Strength of Selected Polymers.....	666
Compressive Strength of Selected Polymers .....	669
Modulus of Elasticity in Flexure of Selected Polymers .....	674
Flexural Strength of Selected Polymers .....	683
Fatigue Strength of Selected Wrought Aluminum Alloys (Listed by Alloy) .....	691
(Listed by Fatigue Strength) .....	695
Coefficient of Static Friction for Selected Polymers .....	699
Abrasion Resistance of Selected Polymers .....	701
Electrical, Magnetic, and Optical Properties .....	705
Electrical Resistivity of Selected Alloy Cast Irons .....	706
Resistivity of Selected Ceramics .....	707
Volume Resistivity of Selected Polymers .....	713
Dielectric Strength of Selected Polymers.....	722
Dielectric Constant of Selected Polymers .....	731
Dissipation Factor for Selected Polymers .....	740
Arc Resistance of Selected Polymers .....	751
Dispersion of Optical Materials at 298 K .....	757
Transmission Range of Glass Ceramics .....	766
Transparency of Selected Polymers .....	770
Refractive Index of Selected Polymers .....	776
Chemical Properties .....	781
Composition of Sea Water .....	782
Anions in Sea Water .....	783
Water Absorption of Selected Polymers .....	784
Flammability of Selected Polymers .....	793

**ATTACHMENT H**

# Materials and Crystallographic Aspects of HT<sub>c</sub>-Superconductivity

edited by

**E. Kaldis**

Laboratorium für Festkörperphysik,  
Eidgenössische Technische Hochschule Hönggerberg,  
Zürich, Switzerland

NATO Science Committee,  
technological knowledge,  
ies.

: in conjunction with the

ing Corporation  
York

: Publishers  
n and London

j, New York, London,

xgraphical references  
ons from international

ii:

SRIN,

etrieval software in  
Technologies Inc.

d of Publishers or



**Kluwer Academic Publishers**

Dordrecht / Boston / London

Published in cooperation with NATO Scientific Affairs Division

Proceedings of the NATO Advanced Study Institute on  
Materials and Crystallographic Aspects of HT<sub>c</sub>-Superconductivity  
Erice, Sicily, Italy  
May 17-30, 1993

A C.I.P. Catalogue record for this book is available from the Library of Congress.

ISBN 0-7923-2773-X

Published by Kluwer Academic Publishers,  
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

Kluwer Academic Publishers incorporates the publishing programmes of  
D. Reidel, Martinus Nijhoff, Dr W. Junk and MTP Press.

Sold and distributed in the U.S.A. and Canada  
by Kluwer Academic Publishers,  
101 Philip Drive, Norwell, MA 02061, U.S.A.

In all other countries, sold and distributed  
by Kluwer Academic Publishers Group,  
P.O. Box 322, 3300 AH Dordrecht, The Netherlands.

*Printed on acid-free paper*

All Rights Reserved

© 1994 Kluwer Academic Publishers and copyright holders as specified on appropriate pages within

No part of the material protected by this copyright notice may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying, recording or by any information storage and retrieval system, without written permission from the copyright owner.

Printed in the Netherlands

## TABLE OF CONTENTS

Preface

Part I: Structural Aspects

*M. Marezio and J. B. Goode*  
A classification of superconductors  
between the Cl and the Cu

*A.W. Hewat*  
Neutron powder diffraction studies of  
superconductors

*T. Egami*  
Local structural changes in  
temperature superconductors

*D. Hohlwein*  
Superstructures in  
superconductors

*V.I. Simonov*  
Accurate X-ray diffraction  
materials

*C. Chaillout and J. B. Goode*  
Structural and magnetic  
properties of

*John B. Goode*  
Electron energy loss  
spectroscopy

*John B. Goode*  
The system La<sub>2</sub>BaCuO<sub>4</sub>

*John B. Goode*  
The n-type cuprates



## TABLE OF CONTENTS

Preface	ix
---------	----

### Part I: Structure and Structure-Properties Relationship

*M. Marezio and C. Chaillout*

A classification of the copper oxide superconductors and the relationship between the CU valence and the superconducting properties	3
---	---

*A.W. Hewat*

Neutron powder diffraction on the ILL high flux reactor and high $T_c$ superconductors	17
--	----

*T. Egami*

Local structural distortion: implication to the mechanism of high temperature superconductivity	45
---	----

*D. Hohlwein*

Superstructures in 123 compounds X-ray and neutron diffraction	65
--	----

*V.I. Simonov*

Accurate X-ray structural investigations of single crystals of high- $T_c$ materials	83
--	----

*C. Chaillout and M. Marezio*

Structural and physical properties of superconducting $\text{La}_2\text{CuO}_{4+\delta}$	129
--	-----

*John B. Goodenough*

Electron energies in oxides	145
-----------------------------	-----

*John B. Goodenough*

The system $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$	161
---	-----

*John B. Goodenough*

The n-type copper oxide superconductors	175
---	-----

appro-

iced or  
photo-  
written

*Shin-ichi Uchida*

Charge dynamics in high  $T_c$  copper oxides

187

*Y. Maeno*

Lattice instabilities and superconductivity in La-214 compounds

203

## Part II: Physics of HTSC

*D. Brinkmann*

Probing crystallographic and materials properties of Y-Ba-Cu-O superconductors by NMR and NQR

225

*Z. Schlesinger, R.T. Collins, L.D. Rotter, F. Holtzberg, C. Feild, U. Welp, G.W. Crabtree, J.Z. Liu and Y. Fang*

Infrared properties of selected high  $T_c$  superconductors

249

*H. Keller*

Probing high-temperature superconductivity with positive muons

265

*T. Schneider*

Extreme type II superconductors: Universal properties and trends

289

*G. Ruani*

IR-excited Raman spectroscopy on HT $_c$  superconductors

311

*I. Morgenstern, J.M. Singer, Th. Hußlein and H.-G. Matuttis*

Numerical simulation of high temperature superconductors

331

*J. Röhler*

Evidence from EXAFS for an axial oxygen centered lattice instability in YBa $_2$ Cu $_3$ O $_{7.5}$ ?

353

*A.M. Hermann, M. Paranthaman and H.M. Duan*

Single crystal growth and characterization of thallium cuprate superconductors - A review

373

## Part III: Flux Pinning, Pinning Centers, Applications

*P.H. Kes*

Flux pinning in high-temperature superconductors

401

*M. Murakami*

Flux pinning of high temperature superconductors and their applications

433

*J. Mannhart, J.G.*  
High- $T_c$  thin films.

*J. Alarco, Yu. Boik  
Z. Ivanov, V.K. Ka  
J. Ramos, E. Stepa*  
Engineered grain b  
applications

## Part IV: Organic

*J. Fink, P. Adelma  
M. Knupfer, M. Me  
and E. Sohmen*  
High-energy spectr  
superconductors

*G. van Tendeloo a*  
Electron microscop  
materials and fuller

*Jack M. Williams, ,  
Urs Geiser, John A  
Eugene L. Venturin*  
Structure-property  
and anion-based (  
use in the design o

## Part V: Phase Dia

*J. Karpinski, K. Co  
and E. Kaldis*  
Phase diagram, syn  
oxygen pressure Pc

*G.F. Voronin*  
Thermodynamic sta

187	<i>J. Mannhart, J.G. Bednorz, A. Catana, Ch. Gerber and D.G. Schlom</i> High- $T_c$ thin films. Growth modes - structure - applications	453
203	<i>J. Alarco, Yu. Boikov, G. Brorsson, T. Claeson, G. Daalmans, J. Edstam, Z. Ivanov, V.K. Kaplunenko, P.-Å. Nilsson, E. Olsson, H.K. Olsson, J. Ramos, E. Stepanov, A. Tzalenchuk, D. Winkler and Y.-M. Zhang</i> Engineered grain boundary junctions - characteristics, structure, applications	471
225	<b>Part IV: Organic Superconductors</b>	
249	<i>J. Fink, P. Adelman, M. Alexander, K.-P. Bohnen, M.S. Golden, M. Knupfer, M. Merkel, N. Nücker, E. Pellegrin, H. Romberg, M. Roth and E. Sohmen</i> High-energy spectroscopic studies of fullerene and cuprate superconductors	493
265	<i>G. van Tendeloo and S. Amelinckx</i> Electron microscopy and the structural studies of superconducting materials and fullerenes	521
289	<i>Jack M. Williams, K. Douglas Carlson, Aravinda M. Kini, H. Hau Wang, Urs Geiser, John A. Schlueter, Arthur J. Schultz, James E. Schirber, Eugene L. Venturini, Donald L. Overmyer and Myung-Hwan Whangbo</i> Structure-property relationships in radical-cation (electron-donor molecule) and anion-based (including fullerenes) organic superconductors and their use in the design of new materials	539
311	<b>Part V: Phase Diagrams of HTSC</b>	
353	<i>J. Karpinski, K. Conder, Ch. Krüger, H. Schwer I. Mangelschots, E. Jilek and E. Kaldis</i> Phase diagram, synthesis and crystal growth of YBaCuO phases at high oxygen pressure $P_{O_2} < 3000$ bar.	555
373	<i>G.F. Voronin</i> Thermodynamic stability of superconductors in the Y-Ba-Cu-O system	585
401		
433		

**ATTACHMENT I**

# PHYSICAL AND MATERIAL PROPERTIES OF HIGH TEMPERATURE SUPERCONDUCTORS

Edited by  
S.K. Malik and S.S. Shah

NOVA SCIENCE PUBLISHERS, INC.

YOUNG

QC  
611  
.98  
H54 P48  
1993

Art Director: Christopher Concannon  
Graphics: Elenor Kallberg and Maria Ester Hawrys  
Book Production: Michael Lyons, Roseann Pena,  
Casey Pfalzer, June Martino,  
Tammy Sauter, and Michelle Lalo  
Circulation: Irene Kwartiroff, Annette Hellinger,  
and Benjamin Fung

*Library of Congress Cataloging-in-Publication Data*

Physical and material properties of high temperature  
superconductors / edited by S.K. Malik and S.S. Shah.  
p. cm.

Includes bibliographical references and index.

ISBN 1-56072-114-6 : \$145.00

1. High temperature superconductors. 2. High  
temperature superconductivity. I. Malik, S.K. II. Shah, S.S.

QC611.98.H54P48 1993

93-8788

537.6'23-dc20

CIP

© 1994 Nova Science Publishers, Inc.  
6080 Jericho Turnpike, Suite 207  
Commack, New York 11725  
Tele. 516-499-3103 Fax 516-499-3146  
E Mail Novasci1@aol.com

All rights reserved. No part of this book may be reproduced,  
stored in a retrieval system or transmitted in any form or by any  
means: electronic, electrostatic, magnetic, tape, mechanical,  
photocopying, recording or otherwise without permission from  
the publishers.

*Printed in the United States of America*

**LIBRARY**  
University Of Miami

# Contents

Preface	xi
Chemistry and Superconductivity of $(\text{Ti,A})(\text{Ba,Sr,Ln})_2(\text{Cu,M})\text{O}_{5\pm\delta}$ 1201 Thallium Cuprates <i>M. Greenblatt and M.-H. Pan</i>	1
Phase Formation and Superconducting Properties of $\text{LnBaSrCu}_3\text{O}_7$ Compounds <i>V. Badri, U.V. Varadaraju, and G.V. Subba Rao</i>	35
Structure and Properties of Electron Superconductors <i>G. Balakrishnan</i>	49
The Influence of Pr and Cm on the Superconducting Properties of High- $T_c$ Oxides <i>L. Soderholm and C.W. Williams</i>	59
Synthesis, Crystal Structure and Physical Properties of the $\text{Pb}_2\text{Sr}_2\text{RCu}_3\text{O}_{8+\delta}$ System <i>J.S. Xue, M. Reedyk and J.E. Greedan</i>	77
Current Directions in the Architecture of High- $T_c$ Superconducting Oxides — A Review <i>Y.V. Yakhmi and R.M. Iyer</i>	121
Characterization of Superconducting Fullerenes <i>J.D. Thompson, G. Sparr, K. Holczer, O. Klein, G. Gruner, R.B. Kaner, F. Diederich, and R.L. Whetten</i>	139
Transport Properties in Y-Doped Bi- and Tl-Based Superconductors <i>B. Ghosh, A. Poddar, P. Mandal, A.N. Das, and P. Choudhury</i>	149
On the Magnitude of Resistivity in High-Temperature Cuprate Superconductors <i>P. Ganguly</i>	163
Chemical Doping and Charge Balance in High Temperature Superconductors <i>E.E. Alp and S.M. Mini</i>	181

- Hidden Aspects of the Valence and Superconductivity  
X. Oudet
- Valence Fluctuation in Metallic and Superconducting Oxides  
M.S. Hegde
- Magnetic Ordering in Oxide Superconductors  
J.W. Lynn
- Rare Earth Magnetism and Superconductivity in  $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$  and  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_7$ : A Neutron Scattering Study  
C.-K. Loong and L. Soderholm
- Magnetism, Superconductivity and Upper Critical Fields in  $\text{R}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  (R = Rare Earth) Compounds  
S.K. Malik and C.V. Tomy
- Low Temperature Specific Heat and AC-Susceptibility of  $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (RE = Y, Nd, Eu, Gd, Dy, Ho, Er, Tm and Yb)  
H. Kierspel, F. Oster, H. Drössler, U. Callies, H. General, H. Geus, G. Jackel, H.D. Jostarndt, J. Langen, A. Waldorf, R. Müller, W. Schlabit, and D. Wohlleben
- Fluctuation Diamagnetic Susceptibility in High Temperature Superconductors  
R. Srinivasan
- Flux-Lattice Melting in High-Temperature Superconductors  
K.N. Shrivastava
- Reversible Magnetization of Copper Oxide Superconductors in the Mixed State  
U. Welp, S. Fleshler, W.K. Kwok, R.A. Klemm, V.M. Vinokur, J. Downey, and G.W. Crabtree
- Vibrating Reed Studies of Flux Line Dynamics in Superconductors  
Lance E. De Long, Zhigang Xu, Ji-Chang Hou and Joseph Brill
- Diffraction from the Flux-Line Lattice in High Temperature Superconductors  
D. McKenzie Paul and T. Forgan
- Measurements on the Flux-Line in Type-I and Type-II Superconductors  
R. Kumar, S. R.
- Quantized Lorentz Force and Resonance in High Temperature Superconductors  
K.N. Shrivastava
- Crystal Growth and Properties of High-Tc Superconductors  
S.C. Gadgari, M.
- Magnetic Properties of High-Tc Superconductors  
Ming Xu
- Recent Theories of High-Tc Superconductivity  
K.P. Sinha
- Critical Current in High-Tc Superconductors  
P. Bhattacharyya
- Critical State Model for Demagnetization of High-Tc Superconductors  
P. Chaddah and
- High-Tc Josephson Junctions  
A.K. Gupta
- Structural, Morphological and Superconducting Properties of High-Tc Superconducting Films of High-Tc Superconductors  
S.B. Ogale, S.M.
- Preparation and Characterization of High-Tc Superconducting Films  
R. Viswanathan,
- In-Situ Growth of Superconducting Films  
R. Pinto
- Preparation and Characterization of High-Tc Superconducting Films  
S.K. Gupta, and



ides	2	Measurements on Inhomogeneous Magnetic States and Irreversibility Line in Type-I and Type-II Superconductors	421
		<i>R. Kumar, S. Ramakrishnan, and A.K. Grover</i>	
	2	Quantized Lorentz Force, Microwave Absorption and Magnetic Resonance in High Temperature Superconductors	445
	2	<i>K.N. Shrivastava</i>	
$\text{CuO}_4$ and	2	Crystal Growth and Characterization of Oxide Superconductors	477
		<i>S.C. Gadkari, M.K. Gupta, and S.C. Sabharwal</i>	
in	2	Magnetic Properties in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ Single Crystals	497
		<i>Ming Xu</i>	
	2	Recent Theories of High $T_c$ Superconductivity	529
		<i>K.P. Sinha</i>	
and Yb)	3	Critical Current in High Temperature Superconductors	541
eral,	3	<i>P. Bhattacharyya</i>	
orf,		Critical State Model for Samples with Non-Zero Demagnetization Factor	557
		<i>P. Chaddah and K.V. Bhagwat</i>	
	3	High- $T_c$ Josephson Junctions—A Review	571
		<i>A.K. Gupta</i>	
	3	Structural, Morphological and Superconducting Properties of the Thin Films of High- $T_c$ Oxide Superconductors Deposited by Pulsed Laser Ablation	591
in the		<i>S.B. Ogale, S.M. Kanetkar, R.D. Vispute,</i>	
'inokur,	3	<i>R. Viswanathan, and S.T. Bendre</i>	
		In-Situ Growth of Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Thin Films	629
		<i>R. Pinto</i>	
ctors	3	Preparation and Characterization of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Thick Films	649
Brill		<i>D.K. Aswal, M.K. Gupta, A.K. Debnath,</i>	
	4	<i>S.K. Gupta, and S.C. Sabharwal</i>	

Containerless Melt Processing of  $\text{REBa}_2\text{Cu}_3\text{O}_{7-x}$  (RE = Y, Gd, Nd)  
High Temperature Superconductors

R.W. McCallum, M.J. Kramer, T.J. Folkerts, S.R. Arrasmith,  
B.D. Merkle, S.I. Yoo, Youwen Xu and K.W. Dennis

Fabrication of High  $T_c$  Oxide Superconductors

R. Prasad, N.C. Soni, K. Adhikary, and S.K. Malik

Influence of Zn, Ni and Co Substitution on Flux-Pinning and Critical  
Current in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

R.G. Kulkarni

Magnetic Resonance Imaging (MRI)—A Programme in Superconductivity

R.S. Chaughule

Subject Index

The idea of this  
temperature Super  
during February 21  
ment of Physics, I  
by the Department  
Institute of Funda  
Aurangabad, and Indi

It was decided  
in the form of a b  
Workshop many to  
was, therefore, felt  
should invite article  
are very happy to r

We are indebt  
and made it self-su  
Science and Techn  
al Research, Mara  
Colleges and Indus

S.K. Malik  
Data Institute of F  
Bombay 400 005, I

S.S. Shah  
Marathwada Unive  
Aurangabad 431 0

**ATTACHMENT J**



ELSEVIER

Physica C 230 (1994) 231–238

PHYSICA C

# Synthesis and characterization of $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ ( $n=1, 2$ , and $3$ )

O. Chmaissem, L. Wessels, Z.Z. Sheng \*

Department of Physics, and High Density Electronics Center, University of Arkansas, Fayetteville, AR 72701, USA

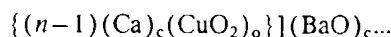
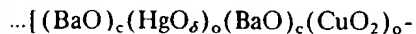
Received 17 May 1994; revised manuscript received 20 June 1994

## Abstract

We have successfully prepared the first three members of the mercury-based superconducting compounds  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ , namely Hg-1201, Hg-1212 and Hg-1223 with high purity and very good quality. The influence of the synthesis parameters is studied in detail. Using the sealed quartz tube method, very simple procedures are found to ensure a 100% reproducibility of nearly 100% pure Hg-1201 and 85–90% Hg-1212 and Hg-1223. Oxygen annealing of the sample Hg-1201 at 300°C for 18 h results in an enhancement of its critical temperature up to 97 K. The symmetry of the first and second members is tetragonal with lattice parameters  $a=3.8831(1)$  Å,  $c=9.5357(2)$  Å, and  $a=3.8624(1)$  Å,  $c=12.7045(2)$  Å, respectively. X-ray diffraction lines of Hg-1223 can be indexed in a tetragonal cell with  $a=3.8564(1)$  Å and  $c=15.8564(9)$  Å as well as in an orthorhombic cell with lattice parameters  $a=5.4537(1)$  Å,  $b=5.4247(1)$  Å, and  $c=15.8505(7)$  Å.

## 1. Introduction

Following the discovery of superconductivity with  $T_c=94$  K in the one-layer  $\text{HgBa}_2\text{CuO}_{4+\delta}$  compound [1], a variety of new mercury cuprates have been synthesized [2–10].  $\text{HgBa}_2\text{CuO}_{4+\delta}$  (Hg-1201) is the first member of the homologous series  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ . The  $T_{c\text{onset}}$  of the first, second and third members are 94 K, 127 K and 134 K, respectively.  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$  are isostructural to the Tl based superconductors  $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$  [11,12] but unlike the thallium compounds the mercury layers are heavily oxygen deficient. The structure of the Hg based superconductors  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$  can be described as a sequence of layers:



in which blocks  $(\text{BaO})_c(\text{HgO}_\delta)_o(\text{BaO})_c$  having the rock-salt structure and a thickness of about 5.5 Å alternate with blocks  $(\text{CuO}_2)_o\{((n-1)(\text{Ca})_c(\text{CuO}_2)_o)\}$  having a perovskite-like structure and an approximate thickness  $[4.00+(n-1)\times 3.16]$  Å. The subscripts o and c indicate if the cation is at the origin or at the center of the mesh in each layer. All Hg-1201 [13,14], Hg-1212 [3] and Hg-1223 [15] are found to crystallize with symmetry of space group  $P4/mmm$ . An orthorhombic symmetry was also proposed by Meng et al. [16] for Hg-1223.

The research conducted on the thallium-based compounds showed that these materials offer a wide variety of possible substitutions on the different sites of their structures. Many compounds were prepared having their  $T_c$  above 100 K. As we mentioned above many new mercury-related compounds were already successfully synthesized with  $T_c$  around 100 K. Fur-

\* Corresponding author.

thermore, Chu et al. [17] found that under very high pressures of about 150 kbar, the third member Hg-1223 becomes superconducting at 153 K. This result was confirmed by Nunez Regueiro et al. [18] who showed that their Hg-1223 samples if pressed to 235 kbar have a  $T_c$  as high as 157 K. As these results have no practical value because of the enormous pressure required, one may speculate that substituting some elements by smaller ions could imitate the effect of the high pressures and increase  $T_c$  to much higher values. The search for such new elements of substitution requires a well-controlled synthesis technique.

The synthesis of the Hg-Ba-Ca-Cu-O superconducting compounds of high purity remained a serious challenge until this date. One of the reasons for the fact that the preparation of these materials is so delicate is the decomposition of the mercury oxide HgO at low temperature (between 500 and 600°C), and by consequence, the formation of the superconducting phases is due to the reaction between vapor and solid. Two major methods were used:

- (1) the high-pressure methods in which the decomposition of HgO is slow, and
- (2) the sealed quartz tube methods.

Several groups reported their success in preparing samples of good quality using the sealed quartz tube method. Using this method, many classical synthesis routes were employed. Meng et al. [16] reported the synthesis of the mercury compounds ( $n=2$  and 3) using an original method in which the Hg vapor is controlled by the insertion of precursor pellets in the sealed quartz tube together with pellets of nominal composition  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ . However, the synthesis of the mercury compounds has proved to be very delicate and requires good control of all the different preparation procedures such as starting materials, heating temperature, heating time, etc. The aim of our work was to study the influence of all these parameters and to find a more convenient method which guarantees to us the high reproducibility of the desired superconducting phases with high purity. We report herein the optimization of the synthesis of samples of good quality and 100% reproducibility using the sealed quartz tube method.

## 2. Experimental

Several methods were tried before we finally succeeded in synthesizing samples of high purity and 100% reproducibility. Attempts were first made to prepare superconducting samples using the single-step method (mixing the high-purity oxides all together) and heating between 750°C and 850°C. The other preparations were all based on the two-step method in which we first prepared precursors of  $\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ . The best precursors were those obtained by mixing  $\text{Ba}(\text{NO}_3)_2$ , CaO and CuO in appropriate amounts corresponding to the stoichiometric formula [19]. The mixture is placed in an alumina crucible and introduced into a preheated furnace at 650°C for 1–2 h, the temperature is then increased to 750°C and maintained for 1–2 h before the temperature is increased to 800–930°C. The sample is heated at this temperature for 16–18 h before being cooled down to room temperature by turning the furnace off. All of the heating cycle is done under a flowing gas of oxygen. The resulting materials are immediately transferred to a dry box. Some of the precursors are pelletized and the remaining powder is mixed with HgO in a molar ratio of 1:1 and then pelletized. Pellets of  $\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  (P) and of  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$  (non-reacted HBCCO) (total weight about 1.8 g) were sealed together in a vacuum quartz tube (0.6 cm inner diameter, 1.0 cm outer diameter, and 8–9 cm long) which was in turn placed in a steel container as a safety precaution against possible explosion and then slowly heated (1–3.5°C/min) to 800–950°C. The temperature was maintained for 3 to 10 h before cooling slowly (1–3.5°C/min.) to 20–600°C. The furnace was then turned off.

The as-prepared samples were subjected to a heating treatment in a flowing gas of oxygen: the samples were introduced into a preheated furnace at 300°C and heated for a period of 18 h. The samples were then pulled out and quenched to room temperature in a dry box.

The samples were characterized using the X-ray diffraction technique, the AC magnetic susceptibility and the resistivity measurements. X-ray experiments were performed on a "Philips 1830" diffractometer with Cu K $\alpha$  radiation and showed that the superconducting phases were the majority phases in all the

samples prepared under the conditions described above together with some impurity phases which may be estimated to be in the order of 5–20%. These impurity phases are mainly  $\text{CaHgO}_2$  and  $\text{CaO}$ . The AC magnetic susceptibility measurements showed that the samples prepared at temperatures above  $900^\circ\text{C}$  and the samples heated for more than 10 h were not superconducting. These experiments also showed sharp transitions from the normal state to the superconducting state with  $\Delta T_c$  in the order of 5 K.

### 3. Results

#### 3.1. Hg-1201

As the first member of the homologous series  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ , Hg-1201 does not contain calcium; its synthesis can be done very easily using our procedures with very good quality and a sharp superconducting transition. The precursor was first heated at  $750^\circ\text{C}$  (1–2 h) and after the total decomposition of the barium nitrate the temperature was raised to  $900^\circ\text{C}$  for 20 h before being pulled out and quenched to room temperature in the dry box. Slow cooling in the furnace gave the same good quality of precursors. The resulting precursor was partially melted and very well crystallized. An appropriate amount of  $\text{HgO}$  was added to the precursor and pelletized. Pellets of both precursor (P) and non-reacted mixture of  $\text{HgO}$ +precursor (HBCCO) were sealed together at a weight ratio (P/HBCCO) of 0.48 and slowly heated ( $3^\circ\text{C}/\text{min}$ ) to  $810^\circ\text{C}$  maintained for 6 h, and then slowly cooled ( $3.5^\circ\text{C}/\text{min}$ ) to  $575^\circ\text{C}$ . The power was then shut off and the furnace was naturally cooled to room temperature.

X-ray diffraction pattern of a Hg-1201 sample prepared under these conditions is presented in Fig. 1 and shows that Hg-1201 is the majority phase ( $>95\%$ ) and that the compound is nearly single phased. The structure is tetragonal with the space group  $P4/\text{mmm}$ , and there is no evidence of any kind of special extinction. The refined cell parameters of the as-synthesized sample are:  $a=3.8831(1) \text{ \AA}$  and  $c=9.5357(2) \text{ \AA}$ .

AC magnetic susceptibility and resistivity measurements (Fig. 2) performed on Hg-1201 samples show a sharp superconducting transition and a zero

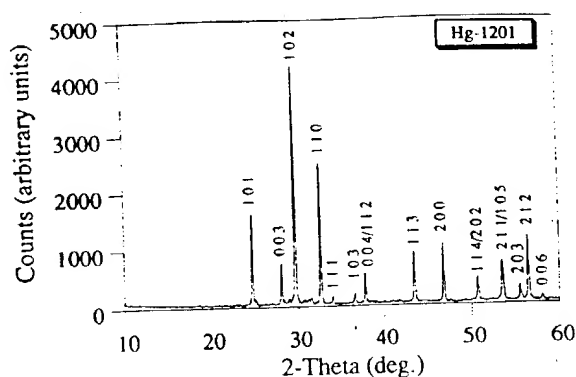


Fig. 1. X-ray diffraction pattern of an as-prepared Hg-1201 sample. The lines are indexed in a tetragonal cell with lattice constants  $a=3.8831(1) \text{ \AA}$  and  $c=9.5357(2) \text{ \AA}$ .

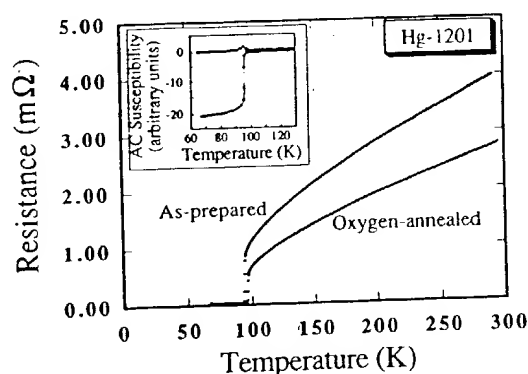


Fig. 2. Resistivity measurements carried out on a Hg-1201 sample. A sharp drop of the resistivity is observed at 94 K in the as-synthesized sample, it increases up to 97 K in the oxygen-annealed sample ( $300^\circ\text{C}$ , 18 h). AC magnetic measurements (real and imaginary parts) are shown in the inset.

resistance at 94 K. Annealing the sample in  $\text{O}_2$  at  $300^\circ\text{C}$  for 18 h results in an increase of its critical temperature up to 97 K. The curves presented in Fig. 2 show the resistivity measurements of the as-prepared and the oxygen-annealed sample. The oxygen-annealed samples were checked by X-ray diffraction and found to be remaining intact with no sign of any apparent change in the structure.

#### 3.2. Hg-1212

With the introduction of the calcium into the structure, the synthesis procedures become more del-

icate and special care should be taken in the different stages of the preparation.

Some groups have reported the successful synthesis of Hg-1212 and Hg-1223 using the single-step method [20-24]. However, their procedures included the preparation of fresh oxides of BaO and CaO and the isolation of the sample from the quartz walls by wrapping the materials with a gold or silver foil [21-23] or even by using alumina tubes to be inserted in the quartz tubes [24]. Our experiments using this method were not successful probably because the samples were introduced in the quartz tubes without wrapping. Unlike the preparations based on the two-step method, the samples are rudely reacted with the quartz even at temperature as low as 750°C and the resulting materials were multi-colored powders with no sign of any homogeneity and particularly no superconductivity.

Our Hg-1212 samples were prepared by repeating the same procedures employed for the synthesis of Hg-1201. The purity of the samples was estimated by both the X-ray diffraction patterns and the AC magnetic-susceptibility measurements. We found that samples prepared at temperatures between 825°C and 860°C contain not more than 65% of the superconducting phase Hg-1212. Table 1 shows the dependence of the Hg-1212 volume percentage on the preparation conditions. The best samples were obtained by heating at relatively low temperature 790°C for 10 h. X-ray diffraction pattern and the superconducting properties are shown in Figs. 3 and 4, respectively. Hg-1212 is also tetragonal with lattice param-

eters  $a=3.8624(1)$  Å and  $c=12.7045(2)$  Å. The  $T_{c\text{onset}}$  of the as-prepared samples is between 110 K and 120 K. Samples annealed in O<sub>2</sub> at 300°C for 18 h have their  $T_{c\text{zero } R}$  increased up to 127 K.

### 3.3. Hg-1223

Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> precursors were prepared by heating the starting materials at 935°C for 7 h. Details are in the experimental section. The first preparations based on these precursors were partially successful as we were able to obtain a superconducting volume in the order of 60%. However, the superconducting phase was Hg-1212 rather than Hg-1223 (according to the X-ray diffraction patterns). Table 2 shows two sets of experiments with detailed synthesis conditions of Hg-1212 from nominal 1223 composition. The upper part of the table concerns the preparations in which the weight ratio P/HBCCO=0. The introduced pellets were only those with the nominal composition Hg<sub>x</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, assuming that the prepared precursors had their initial composition. The mercury oxide was added in excess to the stoichiometric formula in order to compensate the loss resulting from its reaction with the quartz tube. In the lower part of the table are presented the experiments of the Hg controlled vapor by using the method described in the experimental section with the weight ratio P/HBCCO>0. In these preparations the estimated superconducting volume (Hg-1212) is ranging between 0 and 60%. These estimations are based on the X-ray diffraction patterns which also showed

Table 1

Selected experiments carried out for the preparation of Hg-1212. The nominal composition of the precursors used in these experiments is Ba<sub>2</sub>CaCu<sub>2</sub>O<sub>3</sub>. Column 2 gives the weight ratio Precursor/HgBa<sub>2</sub>CaCu<sub>2</sub>O<sub>3</sub>.

Name	Weight ratio	Heating rate (°C/min)	Cooling rate (°C/min)	Temp. (°C)	Time (h)	Hg-1212 vol. (%)
ch26	0.386	3	2→565°C	825	6	65
ch27	0.412	3	2→565°C	845	8	65
ch28	0.388	2.5	1→515°C	860	5	25
ch30	0.257	3	2→515°C	835	6	65
ch31	0.184	3	2→515°C	835	6	65
ch32	0.314	3	2→515°C	835	6	65
ch33	0.398	2	1→565°C	835	6	55
ch34	0.325	2	1→565°C	835	6	50
ch35	0.410	3	2→565°C	790	10	85
ch36	0.210	3	2→565°C	790	10	25

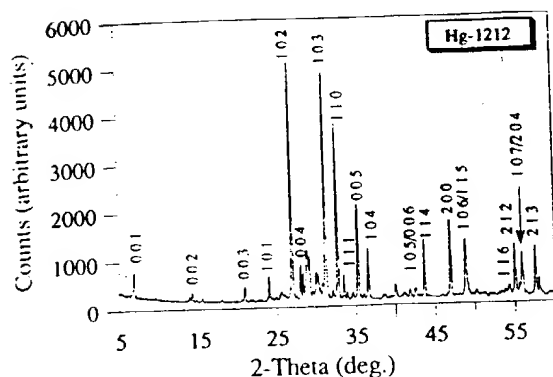


Fig. 3. X-ray diffraction pattern of an as-prepared Hg-1212 sample. The diffraction lines are indexed in a tetragonal cell with the lattice parameters  $a = 3.8624(1) \text{ \AA}$  and  $c = 12.7045(2) \text{ \AA}$ .

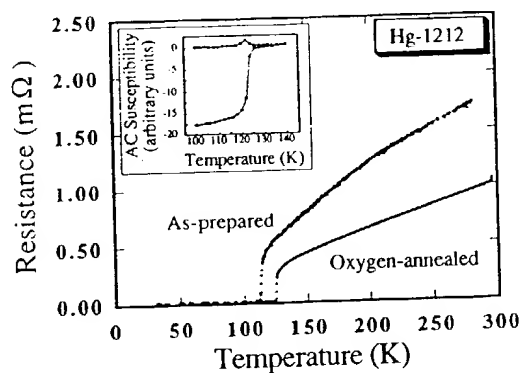


Fig. 4. Resistivity measurements of a sample Hg-1212. The figure shows clearly the increase of the  $T_{c \text{ onset}}$  from 117 K (as-synthesized sample) to 127 K (oxygen-annealed sample). The inset shows the AC magnetic measurements (real and imaginary parts) performed on an oxygen-annealed sample.

that the impurity phases are  $\text{CaHgO}_2$  and  $\text{CaO}$ , with traces of a weak unknown phase. It is clear from the table that the formation of the superconducting phase is favored by the presence of the precursor pellets. The highest superconducting volume is obtained when heating to temperatures close to  $850^\circ\text{C}$ . At  $870^\circ\text{C}$  the sample (ch11) is still superconducting but with a decreased volume down to 40% and the sample is partially melted, indicating that preparations above this temperature could not be carried out successfully.

This work was carried out simultaneously with attempts to synthesize the fourth member of the mercury-based series, namely Hg-1234. The first results showed that the superconducting phase obtained with precursors assumed to be  $\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_9$  (234) was

Hg-1223. By consequence, we started a new series of experiments based on the 234 precursors for the synthesis of Hg-1223.

Nominal  $\text{Hg}_x\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_9$  pellets and  $\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_9$  pellets were sealed together and treated as described in Table 3. Very good Hg-1223 samples with a volume  $\approx 90\%$  were obtained with temperatures between  $870^\circ\text{C}$  and  $885^\circ\text{C}$ . The samples prepared at  $900^\circ\text{C}$  were partially melted and presented only 30 to 40% superconducting volume (samples ch2 and ch5), a longer reaction time at this temperature results in the destruction of the superconducting phase (sample ch19). The reproducibility of the Hg-1223 phase using these procedures is 100%. Using precursors obtained from different batches and following the same conditions given in Table 3 gave 90% Hg-1223 at each time. Together with the superconducting pellets were found drops of mercury inside the closed quartz tube.

X-ray diffraction pattern is given in Fig. 5 which shows the good quality of our Hg-1223 sample. Based on the tetragonal symmetry [4,15] of space group  $P4/\text{mmm}$ , the refined lattice parameters were found to be  $a = 3.8564(1) \text{ \AA}$  and  $c = 15.8564(9) \text{ \AA}$ . During indexing the diffraction pattern we found that many peaks were doubled and cannot all be indexed in the tetragonal symmetry, indicating that the symmetry might be orthorhombic. Refinements in an orthorhombic cell were equally successful and the doubled strong lines were all indexed in a unit cell of lattice parameters  $a = 5.4537(1) \text{ \AA}$ ,  $b = 5.4247(1) \text{ \AA}$  and  $c = 15.8505(7) \text{ \AA}$ .

The AC magnetic susceptibility and the resistivity measurements for a Hg-1223 phasic sample are given in Fig. 6. The  $T_{c \text{ onset}}$  is around 105 K for the as-prepared samples. A  $T_{c \text{ onset}}$  of 135 K can be easily obtained by following the same annealing treatment performed on Hg-1201 and Hg-1212 ( $\text{O}_2$ ,  $300^\circ\text{C}$ , 18 h). The resistivity measurement shows a sharp transition at 135 K and a zero resistance is achieved around 134 K.

#### 4. Discussion

As we stated above, the preparation of Hg-1201, Hg-1212, and Hg-1223 was carried out using the sealed quartz tube method. The insertion of



Table 2

Selected preparation conditions of samples in the phase-formation experiments. The resultant superconducting phase is Hg-1212, and the nominal composition of the precursors is  $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_7$ . Column 2 gives the weight ratio Precursor/ $\text{Hg}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_7$ , where  $x=1$  for the preparation marked with an asterisk and  $x=1.5$  for all the other preparations

Name	Weight ratio	Heating rate ( $^{\circ}\text{C}/\text{min}$ )	Cooling rate ( $^{\circ}\text{C}/\text{min}$ )	Temp. ( $^{\circ}\text{C}$ )	Time (h)	Hg-1212 vol. (%)
Hg1*	0	4	1.5 $\rightarrow$ room temp.	800	8	0
Hg2	0	30	power shut off	850	7	7
Hg3	0	preheated furnace	power shut off	750	7	2
hg12	0	1.5	power shut off	860	8	6
hg16	0	3.5	power shut off	850	5	10
hg11	0.33	4.5	power shut off	850	5	55
hg13	0.35	4.5	power shut off	850	5	55
hg14	0.50	3.5	power shut off	830	5	50
hg15	0.40	2.5	power shut off	850	5	55
hg17	0.26	2.5	power shut off	850	8	65
ch11	0.40	3.5	power shut off	870	5	40

Table 3

Selected experiments carried out for the preparation of Hg-1223. The nominal composition of the precursors used in these experiments is  $\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_x$ . Column 2 gives the weight ratio Precursor/ $\text{Hg}_x\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_7$ , where  $x=1.5$  for the preparations marked with an asterisk and  $x=1.0$  for all the other preparations

Name	Weight ratio	Heating rate ( $^{\circ}\text{C}/\text{min}$ )	Cooling rate ( $^{\circ}\text{C}/\text{min}$ )	Temp. ( $^{\circ}\text{C}$ )	Time (h)	Hg-1223 vol. (%)
ch14	0	1.5	1.0 $\rightarrow$ room temp.	870	5	50
ch10	0.40	3.5	2.5 $\rightarrow$ 600 $^{\circ}\text{C}$	870	5	90
ch15	0.40	3.5	2.5 $\rightarrow$ 600 $^{\circ}\text{C}$	870	5	90
ch16	0.40	3.5	2.5 $\rightarrow$ 600 $^{\circ}\text{C}$	870	5	90
ch13	0.40	3.5	1.5 $\rightarrow$ 550 $^{\circ}\text{C}$	870	5	90
ch17	0.40	3.5	2.5 $\rightarrow$ 600 $^{\circ}\text{C}$	880	8	90
ch18	0.38	3.5	2.5 $\rightarrow$ room temp.	885	5	90
ch19	0.49	1.0	1.0 $\rightarrow$ room temp.	900	10	0
ch4*	0.41	2.5	power shut off	880	10	0
hg1*	0.39	2.5	power shut off	870	8	65
hg3*	0.35	2.5	power shut off	900	5	40
ch2*	0.40	2.5	2.5 $\rightarrow$ 140 $^{\circ}\text{C}$	900	10	40
ch3*	0.42	2.5	power shut off	950	3	0
ch5*	0.40	1.0	power shut off	900	3	30

$\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  pellets (P) together with Hg- $\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  pellets (HBCCO) in the sealed quartz tubes suggests that the total amount of the material inside the tube is mercury deficient. Surprisingly, drops of mercury were observed in almost all the experiments. The formation of Hg-1212 instead of Hg-1223 from nominal 1223 composition and the formation of Hg-1223 instead of Hg-1234 from nominal 1234 composition mean that there are some calcium and copper left.  $\text{CaHgO}_2$  was observed as the major impurity phase and there are negligible traces

of CuO and its related compounds. One may speculate that the copper and the mercury cations are mixed. The substitution of Cu for 8% Hg was observed by Wagner et al. [13] in their Hg-1201 sample. As a consequence, they found additional extra oxygen atoms on the edges of the mercury layer ( $\frac{1}{2}$ , 0, z) together with the already existing extra oxygen atoms at ( $\frac{1}{2}$ ,  $\frac{1}{2}$ , 0). In the first, second, third and fifth member of the mercury-based series the mercury atoms are found to have an unusually high temperature factor [14,15,25-27]. This can be reduced to a more

ase is Hg-1212, and  
 $u_3O_x$ , where  $x=1$  for

Hg-1212 vol. (%)
0
7
2
6
10
55
55
50
55
65
40

n these experiments  
 ked with an asterisk

Hg-1223 vol. (%)
50
90
90
90
90
90
90
0
0
65
40
40
0
30

One may specu-  
 cations are  
 8% Hg was ob-  
 r Hg-1201 sam-  
 additional extra  
 mercury layer ( $\frac{1}{2}$ ,  
 ng extra oxygen  
 l, third and fifth  
 the mercury at-  
 igh temperature  
 duced to a more

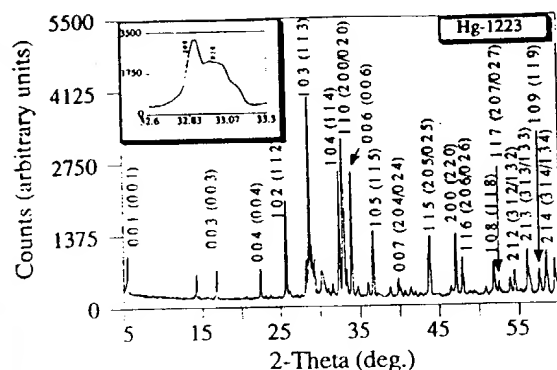


Fig. 5. X-ray diffraction pattern of an as-prepared Hg-1223 sample. The diffraction lines are indexed in both tetragonal cell with lattice constants  $a=3.8564(1)$  Å and  $c=15.8565(9)$  Å and orthorhombic cell (in parentheses) with lattice constants  $a=5.4537(1)$  Å,  $b=5.4247(1)$  Å and  $c=15.8505(7)$  Å. The inset shows the splitting of the line (110) (tetragonal symmetry) into two lines, 200 and 020 (orthorhombic symmetry).

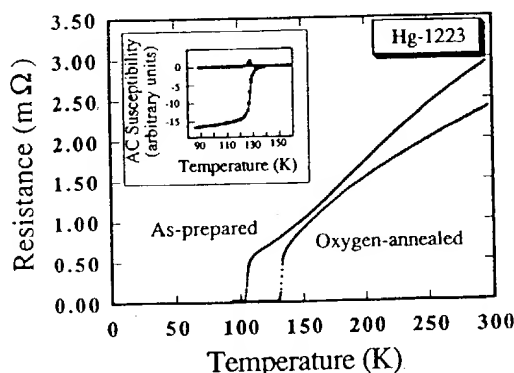


Fig. 6. Resistivity measurements carried out on both as-synthesized and oxygen-annealed Hg-1223 samples. The  $T_{c\text{onset}}$  (originally 105 K) is increased up to 135 K. The curve shows a sharp transition around 135 K with a zero resistance at about 134 K. The real and imaginary parts of the AC magnetic-susceptibility measurements carried out on an oxygen-annealed sample are shown in the inset.

reasonable value by mixing the mercury cations with atoms like copper for example. This possibility was investigated but not proved. The successful preparation of nearly "100%" pure Hg-1201 samples using our method where the mercury cations enclosed in the quartz tube present only 0.57 mole to 1 mole of the precursor  $Ba_2CuO_{3+x}$  confirms that the mixing of Cu and Hg is very possible. The increase of  $T_{c\text{onset}}$  (97 K) might be due to this mixing. However, this conclusion must be interpreted with some caution. A

molar ratio Hg/Cu of 0.57 seems to be rather small compared to 0.85 found by Wagner et al.. Even though our sample looks pure using the X-ray diffraction technique, it might not really be the case. An undetectable (by X-rays) amorphous Ba-Cu-O substance could exist in the powder as well. Such observation was reported by Dolhert et al. [28] who studied the low detectability of excess yttrium and barium in  $YBa_2Cu_3O_7$  by X-ray diffraction. Thus the X-ray "pure" sample may not be actually very pure. However, the formation of  $(Hg, Cu)Ba_2Ca_{n-1}Cu_nO_{2n+2+\delta}$  is possible and seems to be dependent on the preparation conditions. More details need to be studied. As the X-rays are not too sensitive to the oxygen anions, neutron experiments are needed to determine the value of the extra oxygen atoms and their location and to confirm the occupancy of the mercury sites and also to investigate the possibility of any change in the structure.

Our Hg-1223 phase is very likely to be orthorhombic. The orthorhombicity of our samples is observed by the splitting of some of the X-ray diffraction lines. The possibility of the coexistence of two phases with very high rate of overlapped lines would suggest that these two phases are both members of the mercury-based series and by consequence we must be able to observe at least two well-defined superconducting transitions in our measurements. As this was not the case and as the lines (00l) are singles and not split we may conclude that our Hg-1223 phase is orthorhombic. The refined cell parameters are in good agreement with those reported by Meng et al. [16] and Huang et al. [29] for their orthorhombic samples.

## Acknowledgements

We thank John Shultz for his assistance in powder X-ray diffraction. This work was supported by the Advanced Research Projects Agency and the Arkansas Energy Office, USA.

## References

- [1] S.N. Putlin, E.V. Antipov, O. Chmaissem and M. Marezio, *Nature (London)* 362 (1993) 226.

- [2] A. Shilling, M. Cantoni, J.D. Guo and M.R. Ott, *Nature* (London) 363 (1993) 56.
- [3] S.N. Putilin, E.V. Antipov and M. Marezio, *Physica C* 212 (1993) 266.
- [4] E.V. Antipov, S.M. Loureiro, C. Chaillout, J.J. Capponi, P. Bordet, J.L. Tholence, S.N. Putilin and M. Marezio, *Physica C* 215 (1993) 1.
- [5] C. Martin, M. Huve, G. Van Tendeloo, A. Maignan, C. Michel, M. Hervieu and B. Raveau, *Physica C* 212 (1993) 274.
- [6] A. Maignan, C. Michel, G. Van Tendeloo, M. Hervieu and B. Raveau, *Physica C* 216 (1993) 1.
- [7] R.S. Liu, D.S. Shy, S.F. Hu and D.A. Jefferson, *Physica C* 216 (1993) 237.
- [8] F. Goutenoire, P. Daniel, M. Hervieu, G. Van Tendeloo, C. Michel, A. Maignan and B. Raveau, *Physica C* 216 (1993) 243.
- [9] D. Pelloquin, M. Hervieu, C. Michel, G. Van Tendeloo, A. Maignan and B. Raveau, *Physica C* 216 (1993) 257.
- [10] M. Hervieu, G. Van Tendeloo, A. Maignan, C. Michel, F. Goutenoire and B. Raveau, *Physica C* 216 (1993) 264.
- [11] Z.Z. Sheng and A.M. Hermann, *Nature* (London) 332 (1988) 55.
- [12] Z.Z. Sheng and A.M. Hermann, *Nature* (London) 332 (1988) 138.
- [13] J.L. Wagner, P.G. Radaelli, D.G. Hinks, J.D. Jorgensen, J.F. Mitchell, B. Dabrowski, G.S. Knapp and M.A. Beno, *Physica C* 210 (1993) 447.
- [14] O. Chmaissem, Q. Huang, S.N. Putilin, M. Marezio and A. Santoro, *Physica C* 212 (1993) 259.
- [15] O. Chmaissem, Q. Huang, E.V. Antipov, S.N. Putilin, M. Marezio, S.M. Loureiro, J.J. Capponi, J.L. Tholence and A. Santoro, *Physica C* 217 (1993) 265.
- [16] R.L. Meng, L. Beauvais, X.N. Zhang, Z.J. Huang, Y.Y. Sun, Y.Y. Xue and C.W. Chu, *Physica C* 216 (1993) 21.
- [17] C.W. Chu, L. Gao, F. Chen, Z.J. Huang, R.L. Meng and Y.Y. Xue, *Nature* (London) 365 (1993) 323.
- [18] M. Nunez-Regueiro, J.L. Tholence, E.V. Antipov, J.J. Capponi and M. Marezio, *Science* 262 (1993) 97.
- [19] Z.Z. Sheng, Y.F. Li and K.C. Goretti, *Mod. Phys. Lett. B*, to be published.
- [20] P.G. Radaelli, J.L. Wagner, B.A. Hunter, B.A. Beno, G.S. Knapp, J.D. Jorgensen and D.G. Hinks, *Physica C* 216 (1993) 29.
- [21] M. Itoh, A. Tokiwa-Yamamoto, S. Adachi and H. Yamauchi, *Physica C* 212 (1993) 271.
- [22] A. Tokiwa-Yamamoto, K. Isawa, M. Itoh, S. Adachi and H. Yamauchi, *Physica C* 216 (1993) 250.
- [23] W.J. Zhu, Y.Z. Huang, L.Q. Chen, C. Dong, B. Yin and Z.X. Zhao, *Physica C* 218 (1993) 5.
- [24] M. Paranthaman, *Physica C* 222 (1994) 7.
- [25] S.M. Loureiro, E.V. Antipov, J.L. Tholence, J.J. Capponi, O. Chmaissem, Q. Huang and M. Marezio, *Physica C* 17 (1993) 253.
- [26] E.V. Antipov, J.J. Capponi, C. Chaillout, O. Chmaissem, S.M. Loureiro, M. Marezio, S.N. Putilin, A. Santoro and J.L. Tholence, *Physica C* 218 (1993) 348.
- [27] Q. Huang, O. Chmaissem, J.J. Capponi, C. Chaillout, M. Marezio, J.L. Tholence and A. Santoro, *Physica C* 227 (1994) 1.
- [28] L.E. Dolhert and N.D. Spencer, *Mater. Lett.* 9 (1990) 537.
- [29] Z.J. Huang, R.L. Meng, X.D. Qiu, Y.Y. Sun, J. Kulik, Y.Y. Xue and C.W. Chu, *Physica C* 217 (1993) 1.

**ATTACHMENT K**

## The synthesis and characterization of the $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ and $\text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+\delta}$ phases

E.V. Antipov<sup>a,b</sup>, S.M. Loureiro<sup>b</sup>, C. Chaillout<sup>b</sup>, J.J. Capponi<sup>b</sup>, P. Bordet<sup>b</sup>, J.L. Tholence<sup>c</sup>,  
S.N. Putilin<sup>a</sup> and M. Marezio<sup>b,d</sup>

<sup>a</sup> Department of Chemistry, Moscow State University, 119899 Moscow, Russian Federation

<sup>b</sup> Laboratoire de Cristallographie CNRS-UJF, BP 166, 38042 Grenoble Cedex 09, France

<sup>c</sup> CRTBT, CNRS-UJF, BP 166, 38042 Grenoble Cedex 09, France

<sup>d</sup> AT&T Bell Laboratories, Murray Hill, NJ 07974, USA

Received 28 June 1993

Revised manuscript received 9 July 1993

The third (Hg-1223) and the fourth (Hg-1234) members of the recently-discovered homologous series  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$  have been synthesized by solid state reaction, carried out at 950°C under 50 kbar at different annealing times. These phases have a tetragonal cell with lattice parameters:  $a=3.8532(6)$  Å,  $c=15.818(2)$  Å and  $a=3.8540(3)$  Å,  $c=19.006(3)$  Å, respectively. The  $c$  parameters are in agreement with the formula  $c \cong 9.5 + 3.2(n-1)$ . Electron microscopy study showed similar lattice parameters as well as the occurrence of different intergrowths and stacking faults. A periodicity of 22 Å has also been detected, which may be attributed to the existence of the Hg-1245 phase. EDS analysis data of several grains of Hg-1223 and Hg-1234 are in agreement with the proposed chemical formulae. AC susceptibility measurements show that an increase of the superconducting transition temperature with  $n$  in the  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$  series occurs till the third member, after which a saturation seems to be achieved.

### 1. Introduction

Superconductivity at about 94 K and well above 120 K has been recently reported for  $\text{HgBa}_2\text{CuO}_{4+\delta}$  (Hg-1201) [1] and  $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$  (Hg-1212) [2], respectively. These phases are the first and the second members of the Hg-based homologous series of layered Cu mixed oxides. Their structures contain rock-salt-like slabs, such as  $(\text{BaO})(\text{HgO}_\delta)(\text{BaO})$  alternating with either one  $(\text{CuO}_2)$  layer in the former or an anion-deficient perovskite-like slab, such as  $(\text{CuO}_2)(\text{Ca}\square)(\text{CuO}_2)$ , in the latter. A superconducting transition temperature as high as 133 K has been reported for a multiphasic sample in the Hg-Ba-Ca-Cu-O system by Schilling et al. [4]. These authors could not identify by X-ray diffraction the phases responsible for the superconductivity at this temperature, but proved by high resolution electron microscopy that the sample contained the Hg-1212 and Hg-1223 phases as well as different intergrowths. Putilin et al. [2] showed that in the sample

containing Hg-1212 as the majority phase, a small drop on the AC susceptibility curve versus  $T$  occurred at about 132 K which could be attributed to the third member of the Hg-bearing series.

Putilin et al. also showed [2] that it was possible to synthesize the Hg-1212 phase, practically in pure form, under high pressure (40–60 kbar) and at 800°C for about 1 h. The high pressure synthesis allows one to lower the mercury oxide decomposition. This decomposition occurs at ambient pressure at a temperature at which the reactivity of the other components is very low. It was suggested that the same technique could be used for obtaining the higher members of the series. We found that the reactions have to be carried out at higher temperatures (950°C) and for longer annealing times. The same occurs for the higher members of the Bi- or Tl-based Cu oxide series, which are formed by the formation, at the initial stages of the reaction, of the lower members of the corresponding families. We report herein the synthesis and characterization of the Hg-

$\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  (Hg-1223) and  $\text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+\delta}$  (Hg-1234) phases. The reactions were carried out in a belt-type apparatus under high pressure (50 kbar) at 950°C for 3 and 3.5 h, respectively.

## 2. Synthesis and characterization by X-ray and EDS analysis

Powder samples containing the  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  and  $\text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+\delta}$  phases were obtained by high-pressure and high-temperature reactions using the belt-type apparatus of the Laboratoire de Cristallographie. A precursor with the nominal composition  $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  was prepared by mixing high-purity nitrates:  $\text{Ba}(\text{NO}_3)_2$  (Aldrich, >99%),  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Normapur Prolabo, analytical reagent) and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (Strem Chemical Inc., 99.5%). The mixture thus obtained was initially heated at 600°C in air for 12 h, then regrinded and annealed at 925°C for 72 h in an oxygen flow with three intermediate regrindings. Then, the stoichiometric amount of yellow  $\text{HgO}$  (Aldrich, >99%) was added and the mixture was thoroughly grounded in an agate mortar and sealed in a Pt capsule specific for high pressure synthesis. Various temperatures and annealing times at a pressure of 50 kbar were tried in order to obtain the Hg-1223 and Hg-1234 phases. In these experiments the pressure was first increased to 50 kbar, subsequently the temperature was raised to the desired value during 1 h, then the temperature and the pressure were kept constant for 1–4 h. After this, the furnace power was shut off and the pressure decreased to normal conditions in 30 min.

The samples were studied by X-ray powder diffraction, performed with a Guinier focusing camera and  $\text{Fe K}\alpha$  radiation (1.93730 Å). Finely powdered silicon ( $a=5.43088$  Å at 25°C) was used as an internal standard. The intensities of the reflections were evaluated by an automatic film scanner. The SCAN3 and SCANPI programs were used for processing the data [5].

The phase  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  was present in the sample synthesized at 950°C for 3 h (sample I) together with a smaller amount of Hg-1212,  $\text{CaO}$  and  $\text{CuO}$ , and traces of  $\text{CaHgO}_2$  [6] and of an unknown phase whose intensities were less than 4%. The X-ray

diffraction pattern of sample I after background subtraction is shown in fig. 1. The 20 reflections corresponding to Hg-1223 were indexed on a tetragonal cell with lattice parameters  $a=3.8532(6)$  Å,  $c=15.818(2)$  Å. The characteristic 001 reflection is shown in the insert. No systematic absences were observed, leading to space group  $\text{P4}/\text{mmm}$  and one formula per unit cell. The measured value of the  $c$  parameter of Hg-1223 corresponded to the expected value calculated by the formula  $c \cong 9.5 + 3.2(n-1)$  with  $n=3$  [1].

A scanning electron microscope JEOL 840A equipped with an energy-dispersive spectroscopy (EDS) attachment was used for the analysis of the cation composition of the two prepared samples.  $\text{K}\alpha$ -lines were used for the analysis of the Ca and Cu cations, and  $\text{La}$ -lines for the Ba and Hg ones. EDS analysis of several well crystallized and flat grains showed that besides Hg, Ba, Ca, Cu and O no other element was present in the samples. The average metal ratio found for four grains was  $\text{Hg}:\text{Ba}:\text{Ca}:\text{Cu}=13(2):24(1):26(1):38(1)$ , with standard deviations between parentheses. The cation stoichiometry is in good agreement with the expected formula of the Hg-1223 phase.

The lattice parameters of Hg-1212 refined from ten reflections ( $a=3.859(4)$  Å,  $c=12.68(2)$  Å) are in agreement with the data of Putlin et al. [2]. It should be noted that there is severe overlapping between the  $hk0$  reflections of the Hg-1212 and those of the Hg-1223 phases. Moreover, the  $hk4$  reflections of Hg-1212 overlap with the  $hk5$  reflections of Hg-1223. These overlappings did not allow us to determine all the intensities of the two phases. However, the ratio of the intensities of the strongest lines for Hg-1212 (102 and 103) and Hg-1223 (103 and 104) shows clearly that the Hg-1223 is the predominant phase in sample I (fig. 1).

The presence in sample I of the lower member together with the initial oxides,  $\text{CuO}$  and  $\text{CaO}$ , obviously indicates that the formation of Hg-1223 was not complete after a 3 h annealing period. The synthesis carried out at 900°C for 2 h led to the formation of Hg-1212 which was found to be the main phase in the sample together with the starting compounds. These data show that the formation of Hg-1223 occurs through the synthesis of the lower members of the series. The increase of the annealing

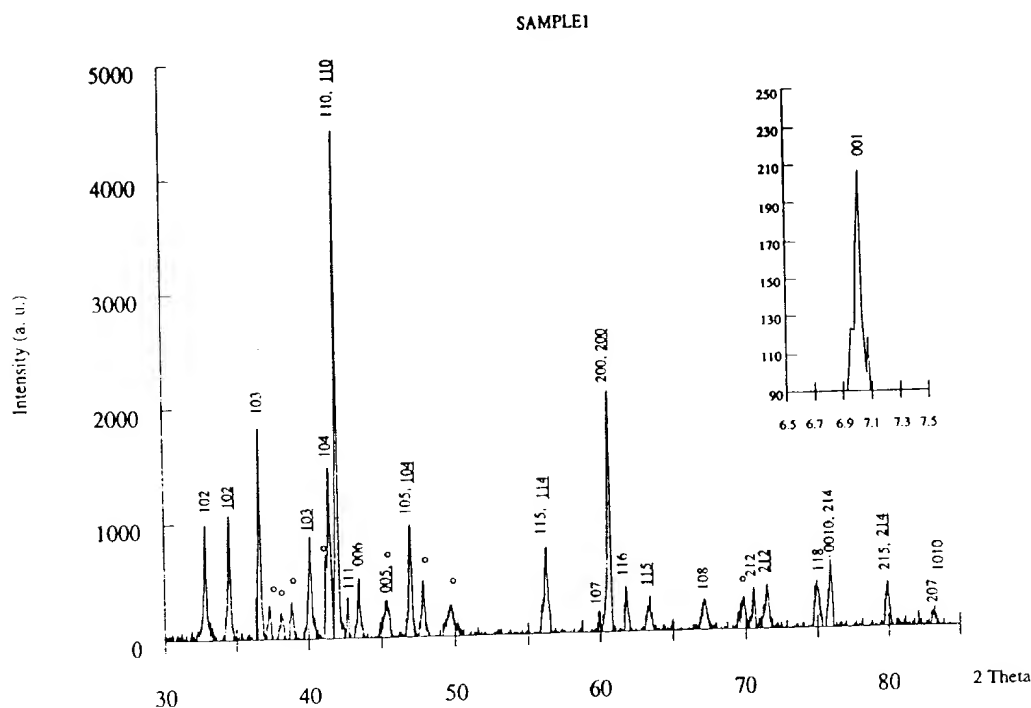


Fig. 1. X-ray powder pattern for sample I. Indexed XRD intensities correspond to Hg-1223 and Hg-1212 (underline). Impurities of  $\text{CaO}$ ,  $\text{CuO}$ ,  $\text{CaHgO}_2$  and an unknown phase are marked by (°). The inset displays the characteristic intensity of 001 for Hg-1223.

time up to 3.5 and 4 h at  $950^\circ\text{C}$  and the same pressure led to the expected disappearance of Hg-1212 as well as of  $\text{CaO}$ . In these samples the formation of a new phase was detected. Its amount was relatively high (more than 50%) in samples annealed for 3.5 h (sample II). A total of 17 reflections of this phase were indexed on a tetragonal cell with lattice parameters  $a=3.8540(3)$  Å,  $c=19.006(3)$  Å. As for Hg-1223 no systematic absences were observed, leading to space group  $P4/mmm$ . Similar parameters were found by electron diffraction (see below). The  $c$  parameters of this phase corresponded to the value calculated from the formula  $c \cong 9.5 + 3.2(n-1)$  for  $n=4$ . This strongly suggested that the new phase was the fourth member of the Hg-based series:  $\text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+x}$ . The approximate cations ratio determined by EDS analysis of five well-crystallized and flat grains was  $\text{Hg}:\text{Ba}:\text{Ca}:\text{Cu}=9(1):18(1):29(2):44(2)$ . These data are in good agreement with the proposed formula for the new compound.

Besides Hg-1234 as the main phase, a smaller amount of Hg-1223 was present in sample II together with small amounts of  $\text{CuO}$  and of an unknown phase. This unknown phase was predominant in a sample treated for 5 h in the same conditions which did not contain any member of the Hg-based series and did not exhibit any superconductivity. The presence of the latter oxides can be explained as a result of the decomposition of Hg-1223 and the formation of Hg-1234. Hg-1212 was absent in this sample as well as in that annealed for 4 h. The X-ray diffraction pattern of sample II after background subtraction is shown in fig. 2. The ratio of the main intensities for both Hg-based layered cuprates, 104 for Hg-1223 and 105 for Hg-1234, shows that the latter was the main phase in this sample. As for sample I the overlapping of  $hk0$  reflections for both phases occurs because of the similarity of the two  $a$  parameters. Moreover, the  $hk6$  reflections of Hg-1234 are overlapped with the  $hk5$  ones of Hg-1223.

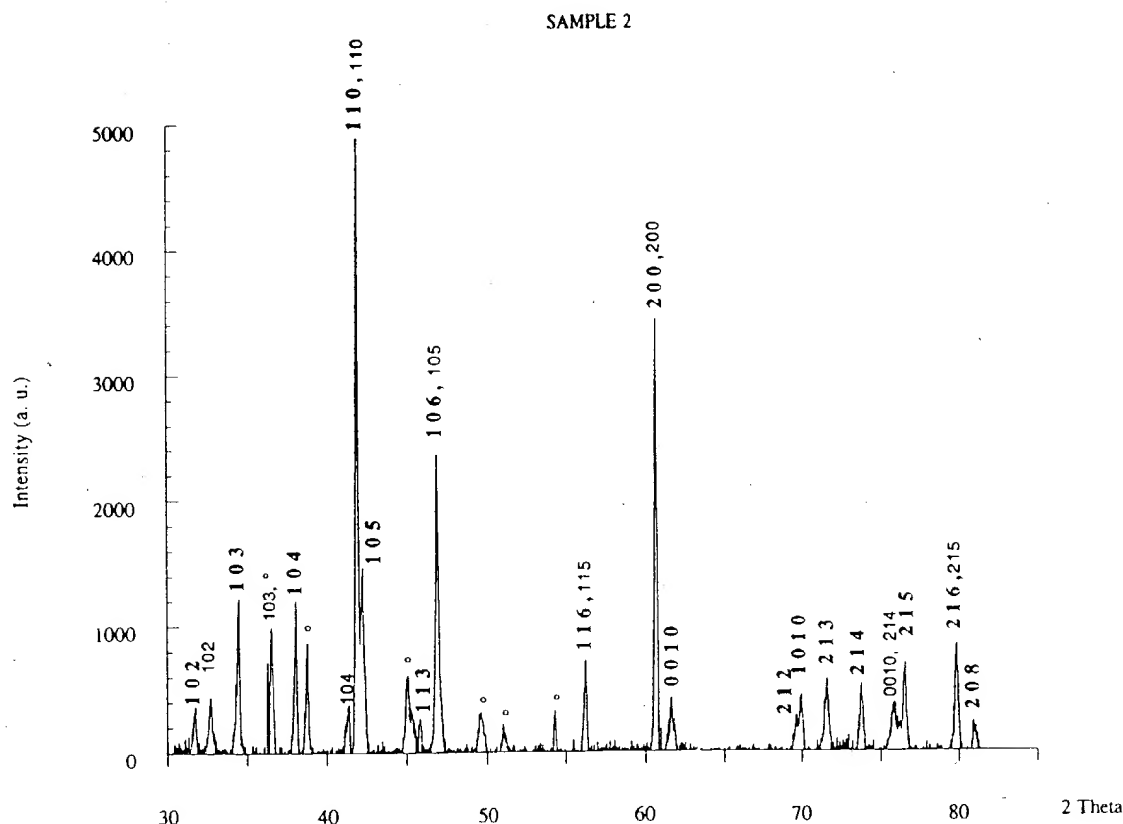


Fig. 2. X-ray powder pattern for sample II. Indexed XRD intensities correspond to Hg-1234 (bold) and Hg-1223. Impurities of CuO and an unknown phase are marked by ( $^{\circ}$ ).

### 3. Electron microscopy

The I and II samples were studied by electron microscopy. A suspension of crystals in acetone was grounded in an agate mortar. The crystallites were recovered from the suspension on a porous carbon film. A Philips EM 400T operating at 120 kV was used.

Figure 3 (a) and (b) shows two diffraction patterns obtained for sample I corresponding to the  $[001]$  and the  $\langle 110 \rangle$  zone axes of the  $\text{Hg-Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  (Hg-1223) phase, respectively. In both cases, the diffraction spots are sharp, which indicates that the crystal is well ordered. In fig. 3(b), one can notice a modulation of the intensity of the diffraction spots along the  $c^*$ -axis, with maxima for  $hkl$  reflections with  $l = 5n$  ( $n = 0, 1, 2, \dots$ ). On the micrograph (fig. 3(c)) corresponding to the diffraction pattern shown in fig. 3(b), one can see the very

regular periodicity of the fringes separated by 15.8 Å. During the observation under the electron beam, dark spots appeared near the edge of the crystal, probably due to the decomposition of the crystal.

Some diffraction patterns obtained for other crystals present diffuse lines parallel to the  $c^*$ -axis and passing through the Bragg spots (fig. 4 (a)). They are due to the presence of intergrowths as given evidence for by fig. 4(b). On this micrograph, two different spacings of 15.8 Å and 12.7 Å can be measured, attributed to Hg-1223 and Hg-1212, respectively.

In the case of sample II, almost all the observed crystallites have diffraction patterns corresponding to the Hg-1234 phase ( $\text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+\delta}$ ) with cell parameters  $a = b = 3.85$  Å and  $c = 19$  Å. Figure 5(a) and (b) give examples of the  $[001]$  and  $\langle 100 \rangle$  zone axes, respectively. As for Hg-1223, also for Hg-1234 the intensity of the Bragg spots varies according to



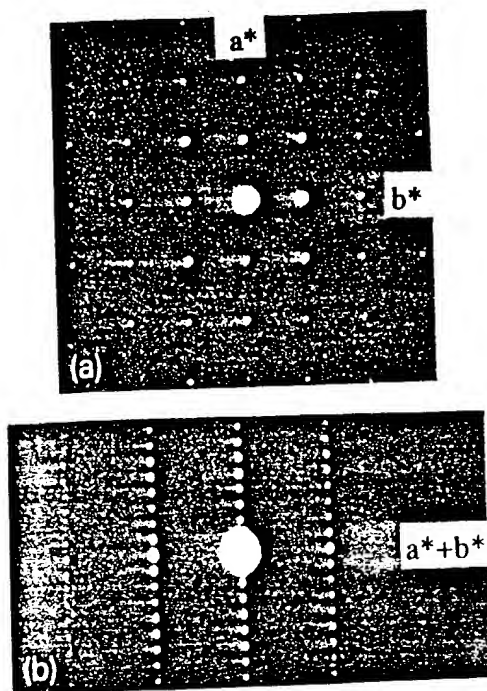


Fig. 3. Electron diffraction patterns of Hg-1223 taken along  $[001]$  (a) and  $[110]$  (b) zone axes. (c) Micrograph corresponding to the diffraction pattern (b). The interfringe spacing is 15.8 Å.

the value of the  $l$  index, the maxima of intensity being obtained for  $l=6n$  ( $n=0, 1, 2, \dots$ ). This intensity pattern might be explained by the fact that  $c/6$  is equal to 3.17 Å, which corresponds to the distance between two neighboring  $(\text{CuO}_2)$  layers. The increase of the layer number  $n$  in the structure leads to the increase of the intensity of the  $hkl$  reflections with

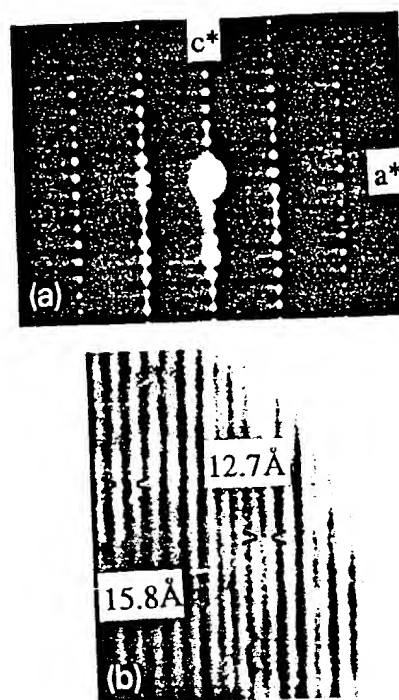


Fig. 4. Electron diffraction pattern of sample I along  $\langle 100 \rangle$  and corresponding micrograph showing the intergrowths of Hg-1223 and Hg-1212.

$l=n+2$ . These periodicities of the  $(\text{CuO}_2)$  layers explain the overlapping of such reflections on the X-ray powder pattern (see above). Most of the images taken along the  $\langle 100 \rangle$  zone axis show very regular fringes separated by 19 Å (fig. 5(c)). However, some crystals present intergrowths between the Hg-1223 and Hg-1234, as revealed in fig. 6. In this case, the following sequence is observed over about 500 Å:  $-19 \text{ Å}-19 \text{ Å}-19 \text{ Å}-19 \text{ Å}-19 \text{ Å}-22 \text{ Å}-$ . On the corresponding diffraction pattern, besides the diffraction spots of the Hg-1234 phase, additional spots related to the 22 Å periodicity are present. Such a periodicity may be attributed to a 1245 phase ( $\text{HgBa}_2\text{Ca}_4\text{Cu}_5\text{O}_{12+\delta}$ ). The fact that the extra diffraction spots are sharp indicates that this phase is well ordered at least over a certain number of cells in these crystals.

#### 4. AC susceptibility measurements

The critical temperature  $T_c$ , and the apparent su-

beta

ns of  $\text{CuO}$

by 15.8  
n beam,  
crystal,  
crystal.  
er crys-  
axis and  
). They  
ven evi-  
two dif-  
be mea-  
Hg-1212,

observed  
ponding  
with cell  
ure 5(a)  
 $\langle 100 \rangle$  zone  
Hg-1234  
ording to

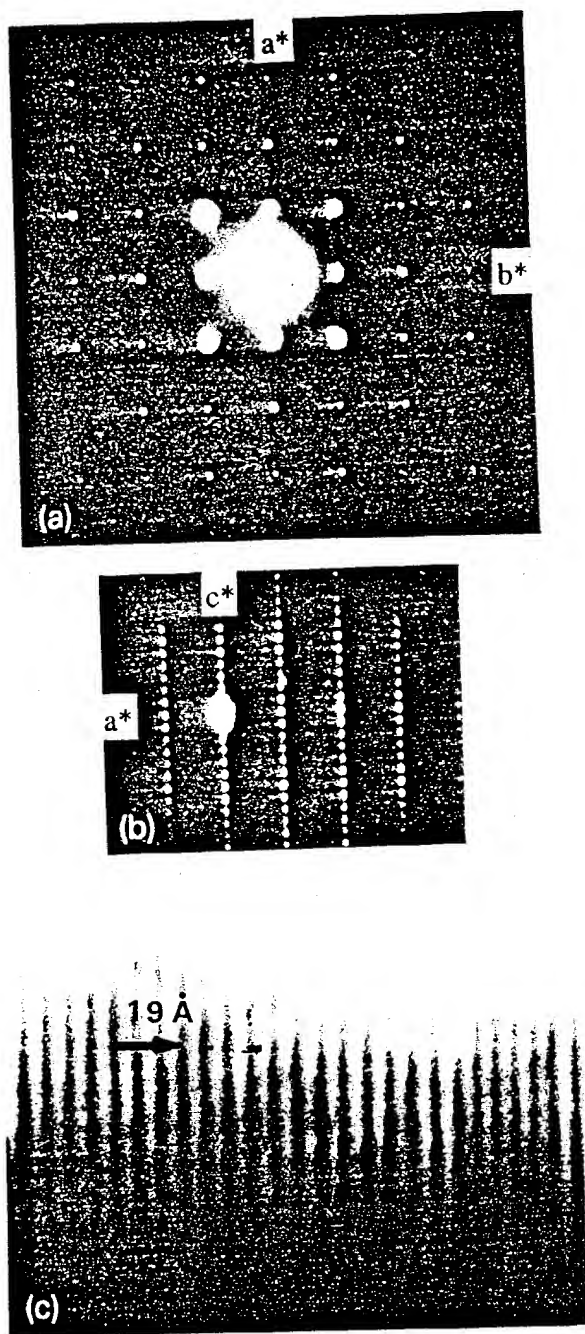


Fig. 5. Electron diffraction patterns of Hg-1234 taken along  $[001]$  (a) and  $\langle 100 \rangle$  (b) zone axes. (c) Micrograph corresponding to the diffraction pattern of (b). The interfringe spacing is 19 Å.

perconducting volume of samples I and II have been determined from AC susceptibility measurements on fine powder samples. This avoids overestimates of the superconducting volume due to the larger screenings in sintered samples. The AC susceptibility was measured with an alternating maximum field of 0.01 Oe and a frequency of 119 Hz. The temperature was measured by a calibrated 100  $\Omega$  platinum thermometer.

The as-synthesized sample I undergoes a transition from the paramagnetic to the diamagnetic state with an onset above 133 K (fig. 7). Several measurements were made with the same sample and the reproducibility of  $T_c$  is  $\pm 1$  K (mainly due to the thermal contact between the sample and the thermometer). The estimated magnetic susceptibility at 4 K corresponds to a large volume of ideal diamagnetism indicating the bulk nature of superconductivity. We can suggest that the sharp and large drop on the AC susceptibility curve above 133 K should correspond to the Hg-1223 phase because Hg-1212, which is present in this sample as the minority phase, has a  $T_c$  not higher than 126 K [3].

The as-synthesized sample II undergoes a transition from the paramagnetic to the diamagnetic state with an onset as high as 132 K. Actually, two onsets at two different temperatures are visible, the smaller one at 132 K and the larger one at about 126 K. There are two Hg-based layered cuprates in this sample: Hg-1234 as the main phase and Hg-1223 as the minority one. Taking into consideration the results of sample I, we might suggest that the first onset (132 K) corresponds to Hg-1223 and the larger one at the lower temperature (126 K) to Hg-1234. In any case, it is obvious that  $T_c$  for Hg-1234 is not higher than that for Hg-1223.

## 5. Discussion

The synthesized  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  (Hg-1223) and  $\text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+\delta}$  (Hg-1234) phases are the third and the fourth members of the  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$  series. In analogy with those of Hg-1201 [1,7,8] and Hg-1212 [2] their structures can be schematized as containing rock-salt-like slabs,  $(\text{BaO})(\text{HgO}_\delta)(\text{BaO})$ , alternating with perovskite-like slabs, consisting in three (Hg-1223) or

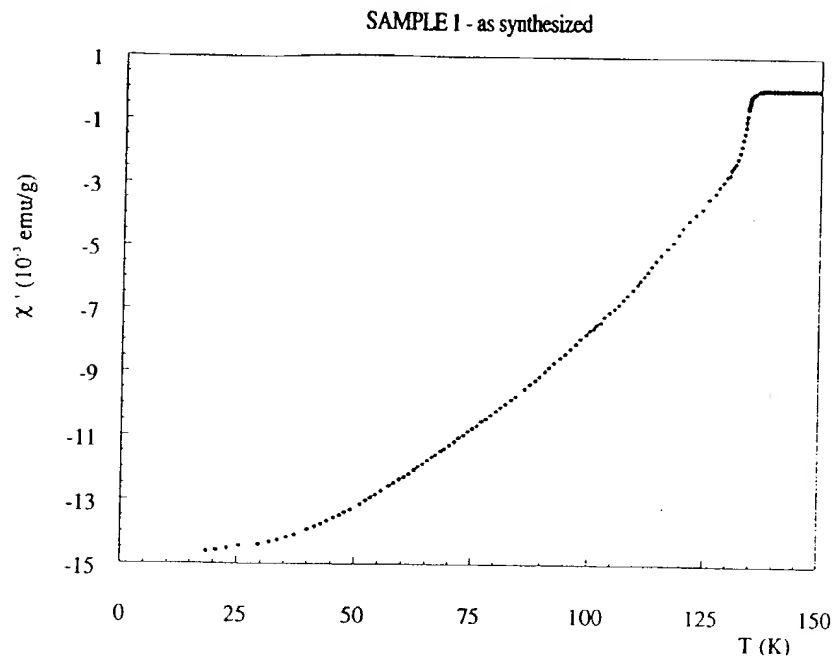


Fig. 7. AC susceptibility vs.  $T$  for as-synthesized sample I, where Hg-1223 is present as the main phase and Hg-1212 as the minority phase.

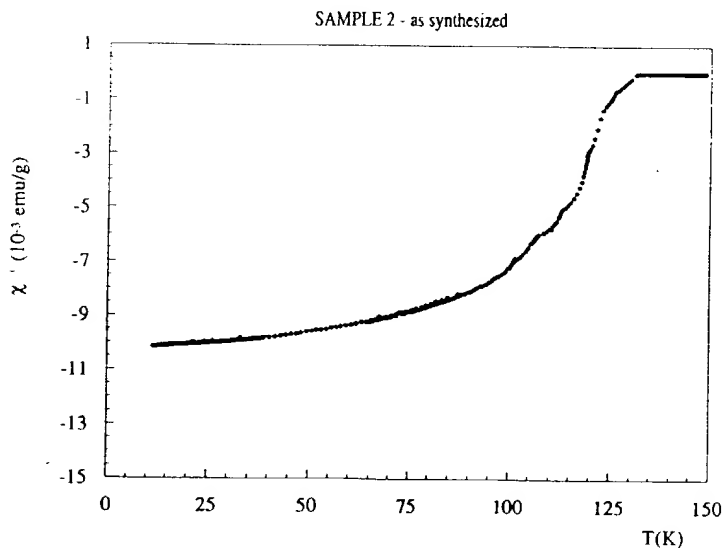


Fig. 8. AC susceptibility vs.  $T$  for as-synthesized sample II showing the presence of Hg-1234 as the main phase and of Hg-1223 as the minority phase.

1212. The appropriate treatment for Hg-1234 can possibly change  $T_c$  for this phase. Therefore, we can only conclude that for the as-prepared samples a saturation of  $T_c$  seems to occur in the Hg-Ba-Ca-Cu-O system at the third member. A similar behavior

occurs for the  $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3+\delta}$  homologous series, for which  $T_c$  increases up to the third member (120 K) also [9].

One can see in table 1 that for the Hg series, the increase of  $T_c$  is accompanied by a decrease of the  $a$

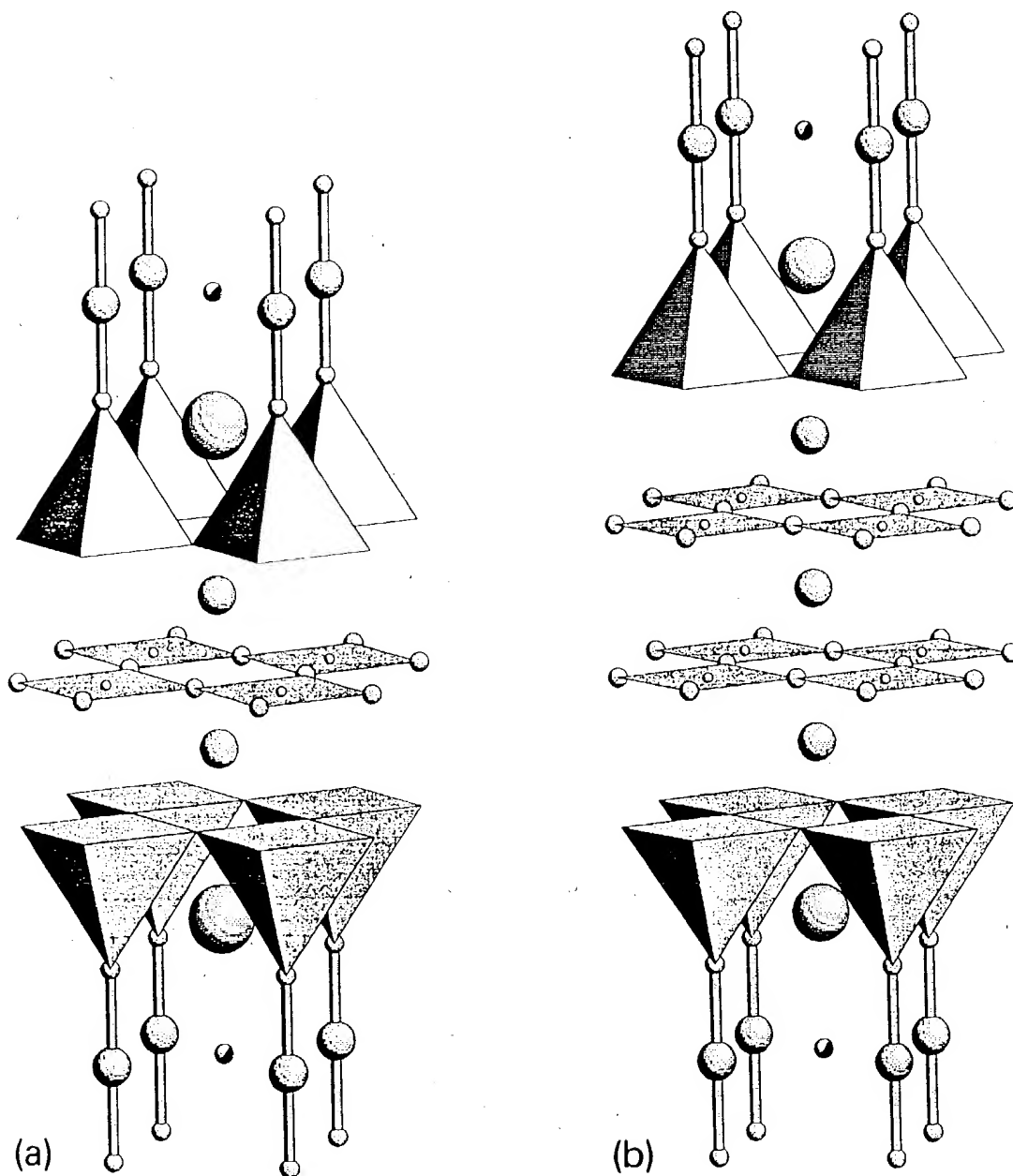


Fig. 9. The crystal structures of Hg-1223 (a) and Hg-1234 (b). The largest and medium large circles refer to Ba and Ca atoms, respectively. The Cu atoms are the smallest circles. Those at the base of the shaded pyramids are not shown. The circles forming the squares around the Cu are oxygen atoms. The dumbbells around the Hg atoms are formed by apical oxygen atoms. Partially filled circles refer to the partially occupied oxygen sites on the Hg layer.

parameter and just at  $T_c$  it remains practically constant between Hg-1223 and Hg-1234.

The electron microscopy study of Hg-1201 [10]

revealed the absence of intergrowths and this was attributed to the absence of the  $\text{Ca}^{2+}$  cations in the system. On the contrary, the addition of Ca layers in

Table I  
Lattice parameters and transition temperatures for Hg-based Cu oxides

Formula	Short form	$a$ (Å)	$c$ (Å)	$T_{\text{c on}}$ (K)	Ref.
$\text{HgBa}_2\text{CuO}_{4+\delta}$	Hg-1201	3.8797(5)	9.509(2)	94	[1]
$\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$	Hg-1212	3.8556(8)	12.652(4)	121	[2]
				126	[3]
$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$	Hg-1223	3.8532(6)	15.818(2)	133	[4], this work
$\text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+\delta}$	Hg-1234	3.8540(3)	19.006(3)	< 132	this work

the system leads to intergrowths due to different numbers of ( $\text{CuO}_2$ ) and Ca layers in the perovskite-like slabs. Such intergrowths were already reported in ref. [4]. Possibly, the occurrence of different intergrowths may explain why the variation versus temperature of the AC susceptibility does not present distinct and abrupt transitions which could be attributed to pure Hg-1212, 1223 and 1234 phases.

The synthesis of the higher members of the Hg-based homologous series as bulk samples has been performed at higher temperatures than that used for Hg-1212 and with longer treatment times. We suggest that the synthesis of such phases occurs through the formation at an initial state and subsequent decomposition of the lower members of the series. This feature is similar to that existing for the  $\text{Tl-Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3-\delta}$  homologous series [9]. The use of high pressure, possibly, lowers the mercury oxide decomposition. It also leads to a decrease of stability of  $\text{CaHgO}_2$ , whose synthesis at the first stage of the reaction inhibits the formation of Hg-based compounds.

#### Acknowledgements

The authors would like to thank M.F. Gorius, M.

Perroux and R. Argoud for their technical assistance. The visit of EVA has been supported by the fund from the French Ministry of Foreign Affairs. EVA and SNP would like to thank the support of the Russian Scientific Council on Superconductivity (Project "Poisk"). SML was supported by the Erasmus Students Exchange Program.

#### References

- [1] S.N. Putlin, E.V. Antipov, O. Chmaissem and M. Marezio, *Nature* (London) 362 (1993) 226.
- [2] S.N. Putlin, E.V. Antipov and M. Marezio, *Physica C* 212 (1993) 266.
- [3] S.M. Loureiro and J.J. Capponi, private communication.
- [4] A. Schilling, M. Cantoni, J.D. Guo and H.R. Ott, *Nature* (London) 363 (1993) 56.
- [5] K.E. Johansson, T. Palm and P.-E. Werner, *J. Phys. E: Sci. Instrum.* 13 (1980) 1289.
- [6] S.N. Putlin, M.G. Rozova, D. Kashporov, E.V. Antipov and L.M. Kovba, *Zh. Neorganicheskoi Khimii* 36 (1991) 1645 (in Russian).
- [7] O. Chmaissem, Q. Huang, S.N. Putlin, M. Marezio and A. Santoro, *Physica C* 212 (1993) 259.
- [8] J.L. Wagner, P.G. Radaelli, D.G. Hinks, J.D. Jorgensen, J.F. Mitchell, B. Dabrowski, G.S. Knapp and M.A. Beno, *Physica C* 210 (1993) 447.
- [9] S. Nakajima, M. Kikuchi, Y. Syono, T. Oku, D. Shindo, K. Hiraga, N. Kobayashi, H. Iwasaki and Y. Muto, *Physica C* 158 (1989) 471.
- [10] I. Bryntse and S.N. Putlin, *Physica C* 212 (1993) 223.

FILING APPELLANT'S REPLY TO THE EXAMINER'S ANSWER WITH  
ATTACHMENTS A, B, & C (3 Sets), AND CERTIFICATE OF MAILING.

DATE OF DEPOSIT: JULY 17, 2000

**PLEASE STAMP & RETURN TO US**

In re application of: BEDNORZ ET AL.

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION ...

Serial No.: 08/303,561; Docket No.: Y0987-074BY Atty.: DPM

Received in the U.S. Patent & Trademark Office: \_\_\_\_\_

No. of pages of specification: \_\_\_\_\_ No. of pages of claims: \_\_\_\_\_

No. of sheets of drawings: \_\_\_\_\_

Declaration is attached to specification..

All fees are charged to our Account No. 09-0468

FILING APPELLANT'S REPLY TO THE EXAMINER'S ANSWER WITH  
ATTACHMENTS A, B, & C (3 Sets), AND CERTIFICATE OF MAILING.

DATE OF DEPOSIT: JULY 17, 2000

**PLEASE STAMP & RETURN TO US**

In re application of: BEDNORZ ET AL.

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION ...

Serial No.: 08/303,561; Docket No.: Y0987-074BY Atty.: DPM

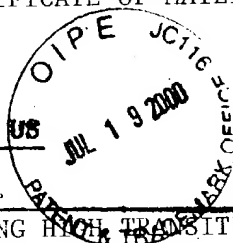
Received in the U.S. Patent & Trademark Office: \_\_\_\_\_

No. of pages of specification: \_\_\_\_\_ No. of pages of claims: \_\_\_\_\_

No. of sheets of drawings: \_\_\_\_\_

Declaration is attached to specification..

All fees are charged to our Account No. 09-0468



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of: Bednorz et al.

Docket No.: YO987-074BY

Serial No.: 08/303,561

Group Art Unit: 1751

Filed: 09/09/94

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

Assistant Commissioner for Patents  
Washington, D.C. 20231

**CERTIFICATE OF MAILING UNDER 37 CFR 1.8 (a)**

I hereby certify that the attached correspondence comprising:

1. Appellant's Reply To The Examiner's Answer  
(With Attachments A, B and C) (3 sets)
2. Acknowledgment Card

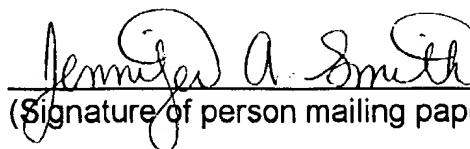
is being deposited with the United States Postal Service as first class mail in an envelope addressed to:

**Assistant Commissioner for Patents  
Washington, D.C. 20231.**

on July 17, 2000

Jennifer A. Smith

(Type or printed name of person mailing paper or fee)

  
(Signature of person mailing paper or fee)

**BEFORE THE BOARD OF PATENT APPEALS  
AND INTERFERENCES**

Paper No. 91

Application Number: 08/303,561

Filing Date: September 09, 1994

Applicants: Johannes G. Bednorz et al.

Daniel P. Morris  
For Appellant

**APPELLANT'S REPLY TO THE EXAMINER'S ANSWER**

**REQUEST FOR REMAND**

Appellants request remand of the present application to the examiner since the examiner introduced a new ground for rejection in the examiner's answer to the appellants' brief.

In the answer at section (10) "Grounds of Rejection" the examiner states:

The following ground(s) of rejection are applicable to the appealed claims:



The specification is objected to under 35 U.S.C. § 112, first paragraph, as failing to provide an enabling disclosure commensurate with the scope of the claims.

The present specification is deemed to be enabled only for compositions comprising a transition metal oxide containing at least a) an alkaline earth element and b) a rare-earth element or Group III B element.

Note that the above 112, first paragraph, rejection has been modified in scope from the Final Office Action. Upon careful consideration of the evidence as a whole, including the specification teachings and examples, and applicant's affidavits and remarks, **the examiner has determined that the instant specification is enabled for compositions comprising a transition metal oxide containing an alkaline earth element and a rare-earth or Group IIIB element (as opposed to only compositions comprising BaLa<sub>1-x</sub>Cu<sub>x</sub>O<sub>y</sub> as stated in the Final Office action).**

Applicant has provided guidance throughout the instant specification that various transition metal oxides (such as copper oxide) containing an alkaline earth element and a rare earth or

Group IIIB element result in superconductive compounds which may in turn be utilized in the instantly claimed methods.

Appellants disagree that they have only enabled compositions containing an alkaline earth element and a rare earth or Group IIIB element to result in superconductive compounds which may in turn be utilized in the instantly claimed methods. This new ground for rejection necessitates the introduction of new evidence to show why the examiners statement is incorrect. There are numerous examples of high Tc superconductors made using the general principals of ceramic science as taught by appellants that existed prior to appellants' earliest filing date. The affidavit of Duncombe submitted by appellants specifically recites some of the compounds reported on in the several hundred pages included from his lab note books which include:  $Y, Ba_2 Cu_3 O_x, Y;$   $Ba_2 Cu_3 O_{3.7}; Bi_{2.15} Sr_{1.98} Ca_{1.7} Cu_2 O_{6.8}; Ca_{(2-x)} Sr_x Cu O_x$  and  $Bi_2 Sr_2 Cu O_x$ . Even though the last three compounds are made according to appellants' teaching they do not come within the scope of the claims allowed by the examiner in the answer since they do not include a rare earth or a group IIIB element. Moreover, in the answer the examiner quotes from the preface of the Poole article which states in part at A3: "The unprecedented worldwide effort in superconductivity research that has taken place over the past two years has produced an enormous amount of experimental data on the properties of the copper oxide type materials that exhibit superconductivity above the temperature of liquid nitrogen. ... During this period a consistent experimental description of many of the properties of the

principal superconducting compounds such as BiSrCaCuO, LaSrCuO, TlBaCaCuO. and YBaCuO has emerged". The first and third of these compositions does not come within the scope of the claims allowed by the examiner in the answer even though Poole states that they are easy to make following the general principals of ceramic science as taught by appellants. Other data supporting appellants view is reported in the Review Article "Synthesis of Cuprate Superconductors" by Rao et al., IOP Publishing Ltd. 1993. A copy of this article is in Attachment C to the reply brief. This article lists in Table 1 the properties of 29 cuprate superconductors made according to appellants teaching. Twelve (#'s 1, 8-13, 16, 17, 20, 21, 27 and 28 ) of those listed do not come within the scope of the claims allowed by the examiner. Only three of the 29 have a  $T_c < 26^\circ\text{K}$ . Those twelve do not contain one or more of a rare earth, a group IIIB element or an alkaline earth element. It is thus clear that broader claims than allowed in the answer should be allowed since it is clear that the allowed claims can be avoided following appellants teaching without undue experimentation. Appellants request remand for the examiner to consider this data in response to the examiner's new ground for rejection.

At page 21 of the answer, the examiner comments in regard to the claims rejected under 35 UCS 112, second paragraph, the examiner states that "[n]ote the Examiner declines to comment on appellants remarks regarding the after-final submissions which have not been entered or considered by the examiner." These unentered after final submissions provide evidence that the

terminology "perovskite-like", perovskite-type", and "rare-earth-like" were understood by persons of skill in the art prior to appellants' filing date. This evidence is in addition to evidence previously submitted to show that these terms were well understood in the art. Thus this new evidence is not directed to any new issues but is additional evidence on the same issue. Prior to the Final Action the undersigned attorney requested the examiner to specify what information was needed to convince the examiner that these terms were well understood in the art. The examiner did not provide any guidance to appellants. Thus a trial and error approach was used to see if what was submitted was sufficient to convince the examiner. The examiner again in the Final Action indicated he was not convinced and appellants submitted additional evidence in the after final submissions. Some of the additional evidence is issued US patents having claims containing the identical terminology which the examiner finds indefinite. Other evidence is issued US patents using similar terminology in issued claims indicates that the use of such terminology in US patent claims is standard USPTO practice. Since the examiner would provide appellants no guidance on what would convince the examiner that these terms were understood by persons of skill in the art, appellants request remand for these after final submissions to be entered and considered.

In addition appellants request remand for the following reasons. After the final action which is the basis of this appeal there was a change in examiner. In the answer the examiner withdrew the prior art rejections over arguments

presented by appellants long before the Final Action. In the answer the rejection under 35 USC 112, first paragraph, was modified to allow broader claims than the single narrow claims allowed in the Final Action. The modification of 35 USC 112, first paragraph, rejection was based on arguments presented by appellants long before the Final Action. Appellants believe that further progress in either resolving all the issues remaining in this appeal or substantially simplifying the issues in this appeal can be made by remanding this application to the new examiner.

**SUMMARY OF ARGUMENT IN THIS REPLY BRIEF**

***THE EXAMINER HAS NOT REBUTTED APPELLANTS  
CLAIM OF PRIORITY***

In the answer the examiner has not rebutted appellants' arguments in support of their claim of priority. Therefore, appellants request the board to grant appellants' claim of priority

***REJECTIONS UNDER 35 USC 102 AND 103 NECESSARILY  
REQUIRES THAT ALL CLAIMS ARE FULLY ENABLED***

The examiner has withdrawn the rejections under 35 USC 102 and 103 over the Asahi Shinbum article since appellants have shown that they conceived prior to the date of this article and were diligent to a reduction to practice. The examiner has not commented on nor rebutted appellants' argument that in rejecting claims under 35 USC 102 and 103 over the Asahi Shinbum article, the examiner necessarily concludes that appellants' claims are fully enabled. The Asahi Shinbum article refers to appellants' work which was reported in their original article which is incorporated by reference in appellants' specification. Since appellants' original article is the only information enabling the Asahi Shinbum article, it logically follows that the examiner necessarily concludes that all appellants' claims are fully enabled.

**OBJECTION TO SPECIFICATION AND REJECTION OF CLAIMS  
UNDER 35 USC 112, FIRST PARAGRAPH  
THE EXAMINER HAS FAILED TO MEET HIS BURDEN OF PROOF**

The only support for the objection to the specification and rejection of claims as not enabled under 35 USC 112, first paragraph, is the examiner's unsupported statement that the field of high T<sub>c</sub> superconductivity is unpredictable, the examiner's unsupported statement that the theoretical mechanism of superconductivity in these materials was not well understood, and three examples in applicants' specification that show metal oxides having a T<sub>c</sub> < 26°K. One of these examples has an onset at 26°K. The examiner provides no extrinsic evidence to support the examiner's position of nonenablement. Applicants have submitted five affidavits of experts rebutting the examiner's position of nonenablement, the article by Rao et al. and the book by Poole et al. which clearly states that it is easy to fabricate high T<sub>c</sub> materials. Moreover, the book by Poole, the Affidavit of Duncombe and the article by Rao shows numerous examples of high T<sub>c</sub> metal oxides fabricated according to appellants' teaching which do not fall within the scope of the claims allowed by the examiner but do fall within the scope of the claims which have not been allowed by the examiner. The examiner has not rebutted appellants' application of case law which holds that 35 USC 112, first paragraph, permits claims to read on inoperable species. Notwithstanding, appellant's claims do not read on any inoperative species. Under *In re Angstadt* 190 USPQ 219, to sustain a rejection

under 35 USC 112, first paragraph, it is the examiner's burden to show that a person of skill in the art must engage in undue experimentation or require ingenuity beyond that expected of a person of skill in the art to practice the claimed invention. According to *In re Wands* 8 USPQ2d 1400, an application does not fail to meet the 35 USC 112 enablement requirement even though experimentation is needed to determine samples useful to practice the claimed invention when the experimentation is not undue. The examiner has not meet his burden under 35 USC 112, first paragraph, as articulated in *In re Angstadt* and *In re Wands*. Moreover under *In re Angstadt*, providing the examples in appellants' specification with a  $T_c < 26^\circ\text{K}$  is commendable frankness and part of appellants' teaching on how to select a high  $T_c$  material. *In re Angstadt* and *In re Wands* hold that a claim is enabled if undue experimentation is not needed to determine if a particular species within the scope of the claim is effective to practice the claimed invention. This is the situation in the present application and the examiner has not rebutted appellants showing that only routine experimentation is needed to fabricate materials useful to practice appellants' invention. It is appellants' view that there can be no question that the record as a whole supports appellants' view that all the claims are fully enabled. Thus, appellants request the board to reverse the rejection to the specification and the rejection of claims under 35 USC 112, first paragraph.



**THE EXAMINER HAS NOT REBUTTED APPELLANTS'  
PROOF THAT THE TERMINOLOGY OF THE CLAIMS REJECTED  
UNDER 35 USC 112, SECOND PARAGRAPH,  
ARE UNDERSTOOD BY PERSONS OF SKILL IN THE ART**

The examiners' rejection of claims as indefinite under 35 U.S.C. 112, second paragraph, for using terminology, such as "rare-earth like", "perovskite-like" and "perovskite-type" is a clear error since there are many issued patents having claims using terminology which is a combination of "-type", and "-like " and there are issued United States Patents having claims including the exact terminology objected to by the examiner. The examiner has given no reasons why the claims in the instant application are indefinite because of terminology using "-type" and "-like" while they are definite in the many cited issued patents. In the answer, the examiner has not rebutted appellants' arguments in the brief. Appellants' have provided extensive proof that this terminology was understood by persons of skill in the art at the time appellants published their original article. Moreover, appellants' original article was published about eight months before the filing date of the first application in the lineage of the present application. Since appellants used this terminology in their original article, the use of this terminology was part of the vernacular of persons of skill in the art and is thus understood by persons of skill in the art as of the earliest filing date of the instant application. The book by Poole

acknowledges this and uses this terminology. Thus appellants request the board to reverse the rejection of claims under 35 USC 112, second paragraph.

## **DETAILED ARGUMENT IN THIS REPLY BRIEF**

### ***Status of Claims***

Claims 24-26, 86-90, 96-177 are pending.

Claim 136 was allowed at the time of Final Rejection. Claims 114-116, 119-121, 124-126, 132, 133, 137, 138, 143, 144, 146, 148, 152-157, 160-163, 167, 168, 171, 172 and 173 have been subsequently allowed in the examiner's answer.

Claims 24-26, 88-90, 96-102, 109-113, 129-131, 134, 135, 139-142, 145, 149-151, 158, 159, 164-166, 169-170 and 174-177 remain rejected under 35 U.S.C. 112, first paragraph.

Claims 86, 87, 96-108, 112, 113, 117, 118, 122, 123, 127, 128 and 147 remain rejected under 35 U.S.C. 112, second paragraph.

### ***Status of Amendments After Final***

In appellant's original Brief filed 7/1/99, at page 4, reference was made to an after-final submission filed 12/14/98. In the Substituted Brief filed 1/18/00 no reference is made to this 12/14/98 after final submission since appellants have determined that the original Brief incorrectly referred to this 12/14/98 after final submission. Accordingly, appellants acknowledge the record to be complete with respect to after-final submissions as delineated by appellant in the Substitute Brief filed 1/18/00. (Hereinafter Brief refers to the Substitute Brief filed 1/18/2000).

### *Issues*

In view of the claims allowed in response to appellant's Substitute Brief, appellants agree with the examiner's new statements of the issues.

Are claims 24-26, 88-90, 96-102, 109-113, 129-131, 134, 135, 139-142, 145, 149-151, 158, 159, 164-166, 169-170 and 174-177 not enabled under 35 U.S.C. 112, first paragraph?

Are claims 86, 87, 96-108, 112, 113, 117, 118, 122, 123, 127, 128 and 147 indefinite under 35 U.S.C. 112, second paragraph?

### ***The 35 USC 102/103 Rejections Withdrawn In View of Appellants Argument Presented Prior to the Final Rejection***

Applicant acknowledge the examiner's statement that "[t]he prior art rejection over Asahi Shinbum, International Satellite Edition (London) November 28, 1986 (hereinafter, "the Asahi Shinbum article") is withdrawn in view of applicant's remarks .... appearing at pages 39-44 of the supplemental response filed 8/5/99." Applicants respectfully submit that the examiner has not withdrawn the rejection but has found the rejection moot in view of the fact that the examiner has agreed that appellant has sufficiently demonstrated conception in the United States before the publication date of the Asahi Shinbum article and diligence to a reduction to practice. Appellants note that on December 3, 1998, Appellants petitioned for withdrawal of the final rejection since the examiner in the Final Action did not respond to Appellants' request for reasons why the examiner did not find that appellants effectively swore behind the date of the

Asahi Shinbum article in the Substitute Amendment dated March 6, 1997. That petition was denied by decision dated February 8, 1999 of Richard V. Fisher, Director Group 1700. The argument presented in the Brief on pages 39-44 in response to which the examiner has withdrawn the 35 USC 102/103 rejections over the Asahi Shinbum article is essentially identical to that presented in the petition to withdraw the Final Rejection and in response filed December 3, 1998. The decision not to withdraw the Final Rejection and not to withdraw the 35 USC 102/103 rejection over the Asahi Shinbum article required that appellants invest substantial time, effort and cost to prepare the argument presented in the Brief at pages 21-51.

***The Examiner Has Not Rebutted Appellants'  
Claim of Priority to the Priority Document***

Appellants disagree with the examiner statement "Accordingly, the issue of claims 24-26, 86-90, 96-135 and 137-177 being supported by the priority document is believed moot in view of the withdrawal of the prior art rejections." Support for claims in a priority document is a separate and distinct issue from whether the claims are anticipated by a reference under 35 USC 102 or obvious over a reference under 35 USC 103. Therefore, the issue of claims 24-26, 86-90, 96-135 and 137-177 being supported by the priority document is not moot in view of the withdrawal of the prior art rejections. Since the examiner did not rebut applicants detailed and specific argument rebutting the examiners view that appellants' claims are not supported by the priority document, appellants

request the board to reverse the examiner and grant applicants claim of priority to the priority document.

### ***Grouping of Claims***

In response to applicants grouping of the claims in the brief the examiner states:

The appellant's statement in the brief that certain claims do not stand or fall together is not agreed with because appellant merely states "Each claim is appealed individually" but fails to present any detailed reasoning in support of such a statement.

Appellants disagree with the examiner that they have failed to present any detailed reasoning in support of their statement that "Each claim is appealed individually." Specific arguments as to each claim are given on pages 114- 173 of the brief. Since the examiner has not commented on nor rebutted any of these arguments, appellants are entitled to have each claim appealed individually.

### ***The Examiner Has Not Rebutted Appellants' Argument That The Prior Art Rejections Necessarily Require That All Of Appellants' Claims Rejected Under 35 USC 120/103 Are Fully Enabled***

In paragraph 9 of the Answer entitled "Prior Art of Record" the examiner states "No prior art is relied upon by the examiner in the rejection of the claims under appeal". Applicants disagree. Claims 24-26, 86-90, 96-135 and 137-177

have been rejected as anticipated under 35 USC 102(a) by the Asahi Shinbum article, and claims 24-26, 86-90, 96-135 and 137-177 have been rejected as obvious under 35 USC 103(a) in view of the Asahi Shinbum article. These rejections have not in fact been withdrawn, but, as stated above, have in fact been found to be moot.

In the Final Action all the claims, except claim 136, were rejected either under 35 USC 102 or 35 USC 103 over the Asahi Shinbum article. Thus in the Final Action, the Examiner is stating that everything within applicants' non-allowed claims rejected under 35 USC 102 over this article, is found in the Asahi Shinbum article and a person of skill in the art can practice the invention of applicants' claims rejected under 35 USC 102 with what is taught in the Asahi Shinbum article alone. Moreover, in the Final Action, the examiner is stating that all the claims rejected under 35 USC 103 over the Asahi Shinbum article alone can be practiced by a person of skill in the art with what is taught in the Asahi Shinbum article in combination with what is known to a person of skill in the art. All of applicants' claims rejected over the Asahi Shinbum article are dominant to (or generic to) the one claim, claim 136, allowed in the Final Action. Thus by stating that all the non-allowed claims are anticipated or obvious over the Asahi Shinbum article alone, the Examiner is stating that a person of skill in the art needs nothing more than what is taught in the Asahi Shinbum article or what is taught therein in combination with what is known to a person of skill in the art to practice that part of each of appellants non-allowed claims which does not

overlap applicants' allowed claim. Thus, it logically follows from the 35 USC 102/103 rejections that all of appellants' claims are fully enabled.

The Asahi Shinbum article states in the first paragraph:

A new ceramic with a very high  $T_c$  of 30K of the superconducting transition has been found. The possibility of high  $T_c$  - superconductivity has been reported by scientists in Switzerland this spring. The group of Prof. Shoji TANAKA, Dept. Appl. Phys. Faculty of Engineering at the University of Tokyo confirmed in November, that this is true.

and in the second paragraph:

The ceramic newly discovered, is an oxide compound of La and Cu with Barium which has a structure of the so-called perovskite and shows metal-like properties. Prof. Tanaka's laboratory confirmed that this material shows diamagnetism (Meisner effect) which is the most important indication of the existence of superconductivity.

The Swiss scientist are the inventors of the present application. Thus this clearly refers to applicants work which was reported in appellants' article which is incorporated by reference in the present application . These passages say that Prof. Tanaka confirmed applicants work. The newly discovered ceramic



referred to in the article is the ceramic reported on in appellants' article. It is thus clear that for the examiner to have rejected appellants claim over the Asahi Shinbum article under 35 USC 102 or 35 USC 103, the examiner necessarily had to find that appellants' article fully enabled their claims.

In the answer the examiner has not commented on nor rebutted these arguments. In appellants' brief at pages 21-22 and at pages 49-51 appellants apply these arguments in detail to the rejection of applicants claims under 35 USC 102 and 35 USC 103, respectively. The examiner, therefore, must be taken to agree with applicants argument in the brief that their teaching has fully enabled all of their claims.

At pages 50-52, at the beginning of appellants' arguments in regard to the objections and rejection based on 35 USC 112, first paragraph, appellants' have repeated these arguments, that is that the 35 USC 102/103 rejections over the Asahi Shinbum article logically requires that all of appellants' claims are fully enabled by appellants' teaching. The examiner has again not responded nor rebutted them. The examiner, therefore, must be taken to agree with applicants argument in the brief that their teaching has fully enabled all of their claims.

The examiners rejections under 35 USC 102 and 103 over the Asahi Shinbum articles have been maintained since the Office Action dated August 26, 1992. Thus the examiner has maintained the view that all of appellants' claims

are fully enabled for about eight years. In view of the fact that the examiner has not rebutted applicants' arguments the Board does not have to consider the examiner's objection under 35 USC 112, first paragraph, that the specification fails to provide an enabling disclosure commensurate with the scope of the claims and the rejections of claims under 35 USC 112, first paragraphs, for lack of enablement.

In summary, all of applicants' claims on appeal, except for claim 136, were originally rejected under 35 USC 102 and/or 103 as being anticipated or obvious over the Asahi Sinbum article which only stated that a professor in Japan reproduced applicants work reported in applicants' published article which was incorporated by reference in the present application. The only logical conclusion from these rejections is that applicants' teaching fully enabled the claims originally rejected under 35 USC 102 and/or 103 which is all of applicants claims except for claim 136. The examiner in the answer has not rebutted this. The examiner has, therefore, conceded, and is estopped from denying, that all of appellants' claims are fully enabled by applicants' teaching.

### ***Grounds For Rejection***

In paragraph 10 of the answer entitled "Grounds of Rejection" the examiner as stated above introduces a new ground for rejection. The examiner states:

The following ground(s) of rejection are applicable to the  
Application 08/303,561

appealed claims:

The specification is objected to under 35 U.S.C. § 112, first paragraph, as failing to provide an enabling disclosure commensurate with the scope of the claims.

In support of this statement the examiner states:

The present specification is **deemed** to be enabled only for compositions comprising a transition metal oxide containing at least a) an alkaline earth element and b) a rare-earth element or Group IIIB element. The art of high temperature (above 30°K) superconductors is an extremely unpredictable one. Small changes in composition can result in dramatic changes in or loss of superconducting properties. The amount and type of examples necessary to support broad claims increases as the predictability of the art decreases. Claims broad enough to cover a large number of compositions that do not exhibit the desired properties fail to satisfy the requirements of 35 U.S.C. 112. Merely reciting a desired result does not overcome this failure. In particular, the question arises: Will any layered perovskite material exhibit superconductivity.

Except for the first sentence which is the new ground for rejection, Appellants have responded in detail to these comments in the brief. A large number of examples are needed to support a broad claim in an unpredictable art only if a person of skill in the art has to engage in undue experimentation to determine embodiments not specifically recited in appellants' teachings. It is the examiner's burden to show that undue experimentation is necessary. The examiner has presented no extrinsic evidence that a person of skill in the art would have to engage in undue experimentation. The examiner has stated without support that the art of high temperative superconductivity is an extremely unpredictable one. Appellants have not merely stated a desired result as clearly shown by the five affidavits submitted by experts in the field, the Poole book and the Rao article. And it is not necessary for any layered perovskite to work to satisfy 35 USC 112, first paragraph, it is only necessary that they can be determined without undue experimentation.

The examiner restates without support that "It should be noted that at the time the invention was made, the theoretical mechanism of superconductivity in these materials was not well understood. That mechanism still is not understood." Appellants note that the theory of superconductivity has been understood for some time. For example, at page 20 of the brief the book by Von Laue is referred to. This book was published in English in 1952 and presents a comprehensive theory of superconductivity. The entire text of this book is

included in Attachment A of this reply brief. Notwithstanding, for a claim to be enabled under section 112, it does not require an understanding of the theory. The examiner then conclusorily states "Accordingly, there appears to be little factual or theoretical basis for extending the scope of the claims much beyond the proportions and materials actually demonstrated to exhibit high temperature superconductivity". This statement is clearly inconsistent with *In re Angstadt* 190 USPQ 219 and *In re Wands* 8 USPQ2d 1400 which hold that to satisfy the first paragraph of 35 USC 112 it is only necessary that a person of skill in the art not exercise undue experimentation to make samples that come within the scope of the applicants claims. Appellants have clearly shown that only routine experimentation is needed to fabricate samples to practice applicants claimed invention. The examiner has not denied, nor rebutted this. The examiner again incorrectly cites *Brenner v. Morrison* stating a "patent is not a hunting license. It is not a reward for the search, but a reward for its successful conclusion". As stated in the brief, this quote applies to utility not to enablement and is thus incorrectly cited by the examiner.

***Reply to Answer Paragraph (11) Entitled "Response to Argument"***

The examiner states:

As discussed above in section 6 Issues, the prior art rejection over Asahi Shinbum, International Satellite Edition (London), November 28, 1986 (hereinafter, "the Asahi Shinbum article") is withdrawn in

view of applicant's remarks. It is believed that the withdrawn of the prior art rejection addresses each of applicant's remarks appearing at pages 7-51 and pages 114-173 of the Substitute Brief filed 1/18/00 (paper #89).

Applicants disagree with the examiner that "that the withdrawn of the prior art rejection addresses each of applicant's remarks appearing at pages 7-51 and pages 114-173 of the Substitute Brief". This is only true in so far as these pages contains arguments in rebuttal of the rejections under 35 USC 102 and 103 which have been rendered moot since the examiner has been convinced by their argument submitted prior to the Final Action that appellants conceived their invention in the United States prior to the date of the Asahi Sinbum article and were diligent to a reduction to practice. As noted above, the examiner has not rebutted applicants argument that the 35 USC 102 and 103 rejections over the Asahi Sinbum article necessarily requires that applicants have fully enabled all their claims. Moreover, pages 114-173 have arguments in support of the patentability of each of the claims. The examiner has not specifically responded nor rebutted any of these specific arguments. Thus, these specific arguments are not rendered moot and must be considered by the Board.

Appellants acknowledge that the rejection under under 35 USC 112, first paragraph, in the Final Office Action, has been modified in scope in the answer. The examiner has determined that the instant specification is enabled for

compositions comprising a transition metal oxide containing an alkaline earth element and a rare-earth or Group IIIB element. Appellants disagree with this. As shown below there are numerous materials made according to appellants' teaching which do not come within the scope of the claims allowed by the examiner in the answer.

The examiner logically inconsistently with the 35 USC 102/103 rejection of appellants' claims objects to appellants' specification and rejects claims as not enabled under 35 USC 112, first paragraph. With respect to the remaining claims rejected under 35 U.S.C. 112, first paragraph, the examiners referring to:

1. appellant's remarks appearing at pages 52-101 of the Substitute Brief;
2. appellants' arguments filed 1/18/00;
3. the Affidavits filed September 29, 1995, January 3, 1996 (paper nos. 49 and 52);
4. the after-final submissions December 15, 1998: (1.132 Declarations of Mitzi, Tsuei, Dinger, Shaw and Duncombe) (Advisory mailed 2/25/99 (Paper 77E))

states they "have been fully considered but they are not **deemed** to be persuasive." (emphasis added)

As noted at page 8 of the specification **deemed** means to have an opinion: believe. The examiner uses the word "deemed" often in the examiner's answer, that is, it is the examiner's opinion or belief unsupported by any factual

evidence. Applicants view is that the examiner's use of the word "deemed" necessarily requires a finding that the examiner has not meet the examiner's burden for establishing a case of lack of enablement since the argument is only based on the examiner's opinion or belief and not on any significant factual evidence. As noted at page 64 of the Brief In re Angstadt states at 190 USPQ 219:

We note that the PTO has the burden of giving reasons, supported by the record as a whole, why the specification is not enabling. In re Armbruster, 512 F.2d 676, 185 USPQ 152 (CCPA 1975). Showing that the disclosure entails undue experimentation is part of the PTO's initial burden under Armbruster; this court has never held that evidence of the necessity for *any* experimentation, however slight, is sufficient to require the applicant to prove that the type and amount of experimentation needed is not undue.

The examiner in the answer has not commented on applicants arguments rebutting the examiner's reasons for non-enablement. The examiner has not satisfied his burden of giving reasons, supported by the record as a whole, why the specification is not enabling. Applicants have provided extensive evidence that to practice applicants claimed invention does not require undue experimentation but only requires routine experimentation. That only routine experimentation is needed to practice applicants claimed invention is shown for example by the affidavits of Mitzi, Dinger, Tsuei, Shaw and Duncombe, the article of Rao et al. and the book of Poole et al. all of which state or show it is



straight forward to use the general principles of ceramic science to make high  $T_c$  transition metal oxide superconductors which is appellants' teaching.

The examiner has not rebutted this but merely **deems** applicants specification to be non-enabling, that is, it is the examiners opinion or belief that applicants specification is nonenabling.

The examiner further states:

The additional case law and arguments by the applicants have been duly noted. For the reasons that follow, however, the record as a whole is **deemed** to support the initial determination that the originally filed disclosure would not have enabled one skilled in the art to make and use the invention to the scope that it is presently claimed. (Emphasis Added)

The examiner has not commented upon nor rebutted appellants' application of these cases to the facts of the present claims on appeal. The examiner merely **deems** (that is in the examiners opinion or belief ) "the originally filed disclosure would not have enabled one skilled in the art to make and use the invention to the scope that it is presently claimed." The examiner presents no intrinsic or extrinsic facts to support the examiner's opinion or belief. The examiner has, therefore, not met his burden "of giving reasons, supported

by the record as a whole, why the specification is not enabling." In re Armbruster, 512 F.2d 676, 185 USPQ 152 (CCPA 1975). Merely stating without evidentiary support that the art of high  $T_c$  superconductivity is unpredictable and stating without support that the theoretical mechanism is not understood does not satisfy the examiner's burden.

The examiner further states:

The applicants quote several passages from their specification at pp. 13-15 of their September 29, 1995 Amendment, but the issue is the scope of enablement, not support. The present disclosure may or may not provide support for particular embodiments, but the issue here is the scope to which that disclosure would have taught one skilled in the art how to make and use a composition which shows the onset of superconductivity at above 26°K. Construed in light of that issue, the invention is not **deemed** to have been fully enabled by the disclosure to the extent presently claimed. (Emphasis Added)

Again the examiner **deems** appellants' claims not enabled. At page 54 of the brief appellants state "Applicants do not have to provide experimental results for every composition that fall within the scope of their claims when a person of skill in the art exercising routine experimentation has a reasonable expectation of success following applicants teaching to achieve a composition through which

can be flowed a superconducting current according to the teaching of Applicants' specification." The examiner has not commented upon nor rebutted this argument. As extensively shown in the brief, it is a matter of routine experimentation to make the compounds which come within the scope of appellants' claims. The examiner has not commented on nor rebutted this. The examiner merely states "Construed in light of that issue, the invention is not **deemed** to have been fully enabled by the disclosure to the extent presently claimed." Again, the examiner is merely stating without any intrinsic or extrinsic evidence that it is the examiners' opinion or belief that the invention is not fully enabled by the disclosure to the extent presently claimed. Again the examiner has not met his burden "of giving reasons, supported by the record as a whole, why the specification is not enabling." In re Armbruster, 512 F.2d 676, 185 USPQ 152 (CCPA 1975).

The examiner further states:

(1) In their September 29, 1995 Amendment, the applicants argue that their disclosure refers to "the composition represented by the formula RE-TM-O, where RE is a rare earth or rare earth-like element, TM is a nonmagnetic transition metal, and O is oxygen", and list several species such as " $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ " which they indicate are found in the present disclosure.

(2) Notwithstanding that argument, it still does not follow that the invention is fully enabled for the scope presently claimed. The claims include formulae which are much broader than the RE-TM-0 formula cited in the disclosure. Claim 24 recites "a transition metal oxide", claim 88 "a composition", and claim 96 "a copper-oxide compound".

Appellants note that their disclosure is not limited to any particular formula as implied by the examiner. See for example the Summary of The Invention which states at page 7, lines 2-5, "In general, the compositors are characterized as mixed transition metal oxide systems where the transition metal can exhibit multivalent behavior".

As stated in the brief at pages 54-55:

According to In re Angstadt 190 USPQ 214, 218 in an unpredictable art, §112 does not require disclosure of a test with every species covered by a claim. The CCPA states:

To require such a complete disclosure would apparently necessitate a patent application or applications with "thousands" of examples or the disclosure of "thousands" of catalysts along with information as to whether each exhibits catalytic behavior resulting in the production of

hydroperoxides. More importantly, such a requirement would force an inventor seeking adequate patent protection to carry out a prohibitive number of actual experiments. This would tend to discourage inventors from filing patent applications in an unpredictable area since the patent claims would have to be limited to those embodiments which are expressly disclosed. A potential infringer could readily avoid "literal" infringement of such claims by merely finding another analogous catalyst complex which could be used in "forming hydroperoxides."

This is exactly the situation in the present application. If applicants are limited to the claims that are allowed by the examiner, a potential infringer could readily avoid "literal" infringement of such claims by merely finding, through routine experimentation, other transition metal oxides having a high  $T_c$ . As shown below there are numerous materials made according to appellants' teaching which do not come within the scope of the claims allowed by the examiner in the answer.

The examiner further essentially repeats what was stated in the Final Action:

The present specification actually shows that known forms of a "transition metal oxide", "a composition", and "a copper-oxide compound" do not show the onset of superconductivity at above

26° K. At p. 3, line 20, through p. 4, line 9, of their disclosure, the applicants state that the prior art includes a "Li-Ti-O system with superconducting onsets as high as 13.7°K." Official Notice is taken of the well-known fact that Ti is a transition metal. That disclosure also refers to "a second, nonconducting CuO phase" at p. 14, line 18.

In response to this appellant stated at page 7 in the brief:

Applicants claims are directed to "transition metal oxides", "a composition" and "a copper-oxide compound" having a  $T_c$  in excess of 26°K which is carrying a superconducting current. Applicants claims do not include in the claimed method compositions having  $T_c < 26^\circ\text{K}$ . Thus the examples on page 3, line 20 - page 4, line 9, are not included in applicants claims. That these are transition metal oxides having  $T_c < 26^\circ\text{K}$  does not mean that Applicants' claims directed to transition metal oxides, compositions and copper oxides having  $T_c > 26^\circ\text{K}$  are not enabled. Applicants provide the teaching on how to fabricate such oxides having  $T_c > 26^\circ\text{K}$ . The "second non-conducting CuO phase" referred to at page 14, line 18, again does not mean that applicants claims are not enabled. Applicants' statements at page 14 is part of applicants teaching on how to achieve an oxide having a  $T_c > 26^\circ\text{K}$ . The Examiner is

attempting to use Applicants' complete description of their teaching to show lack of enablement when, in fact, this complete teaching provides full enablement by showing how samples are and are not to be prepared. Applicants have claimed their invention functionally, that is, as a method of use so the Applicants' claim do not read on inoperable species. What the Examiner "seems to be obsessed with is the thought of [transition metal oxides] which won't work to produce the intended result. Applicants have enabled those of skill in the art to see that this is a real possibility which is commendable frankness in a disclosure."

In re Angstadt, Supra. (Emphasis Added)

The examiner has not commented on appellants citation of In re Angstadt in support of their position which has been presented as bolded and underlined above. The examiner seems to be of the view that the first paragraph of 35 USC 112 requires absolute certainty. As stated in the brief at pages 54-55 according to In re Angstadt 190 USPQ 214, 218 in an unpredictable art, §112 does not require disclosure of a test with every species covered by a claim. In the answer the examiner has not responded nor rebutted appellants' argument.

As stated by appellants in the brief, in particular at page 63, according to In re Angstadt all that is necessary is that the experimentation required to determine which combinations have the desired result (i.e. Tc greater than 26°K)

can be produced without undue experimentation and would not "require ingenuity beyond that to be expected of one of ordinary skill in the art". 190 USPQ, 214, 218 in re Field v. Connover 170 USPQ, 276, 279 (1971).

Appellants have provided extensive evidence that transition metal oxides can be made according to appellants' teaching without undue experimentation and without requiring "ingenuity beyond that to be expected of one of ordinary skill in the art". In the answer, the examiner has not responded to nor rebutted appellants' arguments.

The examiner further states:

Accordingly, the present disclosure is not **deemed** to have been fully enabling with respect to the "transition metal oxide" of claim 24, the "composition" of claim 88,, or the "copper-oxide compound" of claim 96. (Emphasis added.)

Again without facts or acceptable reasons the examiner "**deems**" appellants' claims not enabled and for the reasons given above appellants disagree. Appellants discovered that metal oxides have  $T_c > 26^\circ\text{K}$  that is why they were awarded a Nobel Prize. With respect to the transition metal oxide of claim 24, the "composition" of claim 88 and the "copper-oxide compound" of claim 88, there is no evidence in the record that a person of skill in the art cannot practice the claimed invention without undue experimentation. The only



attempt made by the examiner to factually support the examiner's statement that the claims "are **deemed** not enabled" are the examples provided by appellants which show  $T_c < 26^\circ\text{K}$ . Appellants provide this teaching so that a person of skill in the art will be fully informed on how to practice appellants invention. In this regard the examiner states:

The examples at p. 18, lines 1-20, of the present specification further substantiates the finding that the invention is not fully enabled for the scope presently claimed. With a 1:1 ratio of (Ba, La) to Cu and an x value of 0.02, the La-Ba-Cu-O form (i.e., "RE-AE-TM-0", per p. 8, line 11) shows no superconductivity". With a 2:1 ratio of (Ba, La) to Cu and an x value of 0.15, the La-Ba-Cu-O form shows an onset of superconductivity at " $T_c = 26^\circ\text{K}$ ". It should be noted, however, that all of the claims in this application require the critical temperature ( $T_c$ ) to be "in excess of  $26^\circ\text{K}$ " or "greater than  $26^\circ\text{K}$ ".

Appellants note that examiner states that "the present specification **further substantiates** the finding that the invention is not fully enabled" (Emphasis added) misrepresents the examiner's argument up to this point since up to this point the examiner has only used the unsupported statements that the theory of high  $T_c$  art is very unpredictable and that the theory of high  $T_c$  in these

materials is not understood. These unsupported statements do not substantiate anything and should be disregarded by the Board.

Appellants note that the examiner cites 3 examples from applicants' specification which are transition metal oxides which do not have a  $T_c > 26^\circ\text{K}$ : 1) a Li-Ti-O system with superconducting onsets as high as  $13.7^\circ\text{K}$  ( cited at p. 3, line 20, through p. 4, line 9) , 2) the 1:1 ratio with an  $x=0.02$  sample cited on page 18, line 7, which did not show superconductivity, and 3) the 2:1 composition with  $x=0.15$  with a resistivity drop that occurs at  $26^\circ\text{K}$ . In appellants view the examiner is making a specious argument in regards to the third example. Thus there are only two examples upon which the examiner is "**deeming**" applicants claims not enabled. The examiner seems to be of the view that an applicants' must have 100% predictability. Appellants and the courts disagree. The fact that there are transition metal oxides having  $T_c < 26^\circ\text{K}$  does not mean that applicants have not fully enabled their claimed invention. If only routine experimentation is needed to determine which transition metal oxides have  $T_c > 26^\circ\text{K}$ , without requiring ingenuity beyond that to be expected of one of ordinary skill in the art, then applicants' disclosure enables applicants' claims. In the brief at page 65 appellants note that In re Angstadt states at 190 USPQ 219:

We note that the PTO has the burden of giving reasons, supported by the record as a whole, why the specification is not

enabling. In re Armbruster, 512 F.2d 676, 185 USPQ 152 (CCPA 1975). **Showing that the disclosure entails undue experimentation is part of the PTO's initial burden under Armbruster; this court has never held that evidence of the necessity for any experimentation, however slight, is sufficient to require the applicant to prove that the type and amount of experimentation needed is not undue. ... Without undue experimentation or effort or expense the combinations which do not work will readily be discovered and, of course, nobody will use them and the claims do not cover them. The [examiner] wants appellants to make everything predictable in advance, which is impracticable and unreasonable. ... The key word is "undue," not "experimentation." (Emphasis Added)**

The examiner has not commented on nor rebutted this argument. The examiner's statement that "the present disclosure is not **deemed** to have been fully enabling" is not sufficient to meet the examiner's burden under In re Armbruster and the examiner has thus failed to establish that applicants claims are not enabled. "Appellants do not have to make everything predictable in advance" where, as here, the experimentation to make samples that can be used within the scope of the appellants' claims is not undue.

The examiner further states:

The applicants also have submitted three affidavits attesting to the applicants' status as the discoverers of materials that superconduct  $> 26^{\circ}\text{K}$ . Each of the affidavits further states that "all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar manner (way)". Each of the affidavits add "(t)hat once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above  $26^{\circ}\text{K}$ , such a person of skill in the art, using the techniques described in the (present) application, which includes all known principles of ceramic fabrication, can make the transition metal oxide compositions encompassed by (the present) claims ... without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art." All three affiants apparently are the employees of the assignee of the present application. Those affidavits do not set forth particular facts to support the conclusions that all superconductors based on the work behave in the same way and that one skilled in applicants' work behave in the same way and that one skilled in the art can make those superconductors without undue experimentation. Conclusory statements in an affidavit or specification do not provide the factual evidence needed for patentability.

The examiner has incorrectly stated that appellants have produced three affidavits. Appellants have produced five affidavits of affiants who are employed at the IBM, Thomas J. Watson Research Center. The affidavits of Shaw and Duncombe were reviewed and considered in paper 77E, page 2 and are referred to at page 10 of the answer. The affidavits of Mitzi, Dinger, Tsuei, Shaw and Duncombe and the book of Poole et al. state it is straight forward to use the general principles of ceramic science to make high  $T_c$  transition metal oxide superconductors following appellants' teaching. The book of Poole et al. and the affidavit of Duncombe show numerous example of high  $T_c$  superconductors produced according to applicants teaching. The affidavits of Shaw and Duncombe cites numerous books and articles which provide the general teaching of ceramic science at the time of and prior to the filing date of the present application. The affidavit of Duncombe also provides several hundred pages copied from Mr. Duncombe's notebooks starting from before appellants' filing date showing the fabrication of numerous samples. In regards to these pages, Mr. Duncombe states "I have recorded research notes relating to superconductor oxide (perovskite) compounds in technical notebook IV with entries from November 12, 1987 to June 14, 1998 and in technical notebook V with entries continuing from June 7, 1988 to May 1989." Mr. Duncombe's affidavit list some of the compounds prepared using the general principles of ceramic science:  $Y_1 Ba_2 Cu_3 O_x$ ;  $Y_1 Ba_2 Cu_3 O_3$ ;  $Bi_{2.15} Sr_{1.98} Ca_{1.7} Cu_2 O_{\delta+8}$ ;  $Ca_{(2-x)} Sr_x Cu O_x$  and  $Bi_2 Sr_2 Cu O_x$ . Appellants note that the last three examples do not come within the scope of the claims allowed by the examiner in the answer since

they do not contain a rare earth or group III B element. The examiner has not commented on the data in Mr. Duncombe's affidavit. Mr. Duncombe's affidavit provides direct evidence that these examples were made following appellants' teaching without undue experimentation. Moreover, in the answer the examiner quotes from the preface of the Poole article which states in part at A3 : "The unprecedented worldwide effort in superconductivity research that has taken place over the past two years has produced an enormous amount of experimental data on the properties of the copper oxide type materials that exhibit superconductivity above the temperature of liquid nitrogen. ... During this period a consistent experimental description of many of the properties of the principal superconducting compounds such as BiSrCaCuO, LaSrCuO, TlBaCaCuO. and YBaCuO has emerged". The first and third of these compositions does not come within the scope of the claims allowed by the examiner in the answer since they do not contain a rare earth or group III B element, even though Poole states that they are easy to make following the general principals of ceramic science as taught by appellants. Other data supporting appellants view is reported in the Review Article "Synthesis of Cuprate Superconductors" by Rao et al., IOP Publishing Ltd. 1993. A copy of this article is in Attachment C to the reply brief. This article lists in Table 1 the properties of 29 cuprate superconductors made according to appellants teaching. Twelve (#'s 1, 8-13, 16, 17, 20, 21, 27 and 28 ) of those listed do not come within the scope of the claims allowed by the examiner. Only three of the 29 have a  $T_c < 26^\circ\text{K}$ . Those twelve do not contain one or more of a rare earth,

a group IIIB element or an alkaline earth element. It is thus clear that broader claims than allowed in the answer should be allowed since it is clear that the allowed claims can be avoided following appellants teaching without undue experimentation. Appellants are entitled to claims which encompass these materials since they were made following appellants' teaching.

The article of Rao et al. in the first sentence of the introduction citing appellants' article - which is incorporated by reference in their application - acknowledges that appellants initiated the field of high T<sub>c</sub> superconductivity. Appellants further note that the Rao article acknowledges that "a large variety of oxides" are prepared by the general principles of ceramic science and that appellants discovered that metal oxides are high T<sub>c</sub> superconductors. Citing reference 5 therein - the book "New Directions in Solid State Chemistry", Rao et al. 1989 (Cambridge; Cambridge University Press) for which there is a 1986 edition which predates appellants filing date Rao (See Attachment B) - Rao et al. states:

Several methods of synthesis have been employed for preparing cuprates, with the objective of obtaining pure monophasic products with good superconducting characteristics [3, 4]. The most common method of synthesis of cuprate superconductors is the traditional ceramic method which has been employed for the preparation of a large variety of oxide materials [5]. Although the

ceramic method has yielded many of the cuprates with satisfactory characteristics, different synthetic strategies have become necessary in order to control factors such as the cation composition, oxygen stoichiometry, cation oxidation states and carrier concentration. Specifically noteworthy amongst these methods are chemical or solution routes which permit better mixing of the constituent cations in order to reduce the diffusion distance in the solid state [5, 6]. Such methods include coprecipitation, use of precursors, the sol-gel method and the use of alkali fluxes. The combustion method or self-propagating high-temperature synthesis (SHS) has also been employed.

Reference 5 is another example of a reference to the general principles of ceramic science incorporated into appellants teaching. The Rao et al. article states that the 29 materials reported on in the article and fabricated in Table 1 are fabricated using the general principles of ceramic science. Moreover, the Rao article states that these materials are fabricated by what the Rao article calls the “ceramic method” which is the preferred embodiment in appellants specification, yet 12 of the 29 materials in Table 1 do not come within the scope of the claims allowed by the examiner in the answer. Thus known examples fabricated according to appellants’ teaching will not be literally infringed by the Rao, Duncombe and Poole examples.



The examiner further states:

Those affidavits do not overcome the non-enablement rejection.

The present specification discloses on its face that only certain oxide compositions of rare earth, alkaline earth, and transition metals made according to certain steps will superconduct at  $> 26^{\circ}\text{K}$ .

As stated above, In re Angstadt 190 USPQ 214, 218 held that in an unpredictable art, §112 does not require disclosure of a test with every species covered by a claim. As stated above, appellants note that the examiner has presented no extrinsic evidence that the art of high  $T_c$  superconductivity is unpredictable. It is the examiner's burden to show that a person of skill in the art would have to engage in undue experimentation to practice applicants' claimed invention. The examiner has clearly not done this. The only evidence that the examiner offers in support of his determination of nonenablement are three examples of metal oxide with  $T_c < 26^{\circ}\text{K}$  which the appellants with commendable frankness have included in their specification. Appellants also note, as stated above, there are many other materials made according to appellants' teaching reported in the literature made following appellants teaching which do not come within the scope of the claims allowed in the examiner's answer.

The examiner further states:

Those affidavits are not **deemed** to shed light on the state of the art and enablement at the time the invention was made. One may know now of a material that superconducts at more than 26°K, but the affidavits do not establish the existence of that knowledge on the filing date for the present application. Even if the present application "includes all known principles of ceramic fabrication", those affidavits do not establish the level of skill in the ceramic art as of the filing date of that application.

The examiner stated to the contrary in paper 77E page 2, that "It is the examiner's maintained position that [the] general principles a ceramic fabrication were most certainly known prior to the filing date of the instant application." Thus the examiner acknowledges that the general principles of ceramic science were known prior to appellants filing date. There is no evidence in the record to indicate that anything more is needed to fabricate compositions which can be used to practice applicants' invention to the full scope that it is claim ed in the present invention. To the contrary, appellants have shown numerous examples in the affidavits and references of samples fabricated according to appellants' teaching useful to practice their claimed invention. Notwithstanding, since the claims are method of use claims, appellants do not believe that they are required to provide a teaching of how to fabricate all compositions which may be used within the full scope of applicants' claimed invention.

The examiner acknowledges that the applicants are the pioneers in high temperature metal oxide superconductivity. However, the examiner states "The finding remains, nonetheless, that the disclosure is not fully enabling for the scope of the present claims". The examiner has not commented on appellants' comments in the brief that once applicants discovered high Tc in metal oxides, it was straight forward for others following appellants' teaching to make other examples of high Tc metal oxides. That appellants were the pioneers in Tc metal oxides is not the only issue. The relative ease of making other metal oxides is equally important. Applicants discovery is that metal oxides had high Tc. The fabrication techniques are not applicants discovery since these techniques, as acknowledged by the examiner, were well known prior to applicants discovery.

The examiner has cited seven decisions as providing the legal basis for this determination of non-enablement. In the brief appellants have extensively shown how these seven cases support appellants' position that they have fully enabled their claims. In the answer, the examiner has not rebutted appellants' extensive analysis of these cases and how they apply to the present invention to support appellants' view that appellants' claims are fully enabled. The examiner has not rebutted appellants arguments as to how the examiner has misapplied these cases to the present application. The examiner states "That case law speaks for itself". Applicants agree that the case law speaks for itself, that is, it

supports appellants' position that their claims are fully enabled. The examiner apparently means by this statement that the case law supports the examiner's position that the rejected claims are not enabled. The examiner has not attempted to show how the facts of the cited cases relate to the facts of the present application. The examiner has essentially taken statements out of context from these cases to support the examiner's view. However, when the cases are analyzed as appellants have done in the brief, it is clear that these cases support appellants view that their claims are fully enabled.

The MPEP SECTION---2164.01(a) entitled "Undue Experimentation Factors" citing In re Wands 8USPQ2d 1400 states:

There are many factors to be considered when determining whether there is sufficient evidence to support a determination that a disclosure does not satisfy the enablement requirement and whether any necessary experimentation is "undue." These factors include, but are not limited to:

- (A) The breadth of the claims;
- (B) The nature of the invention;
- (C) The state of the prior art;
- (D) The level of one of ordinary skill;
- (E) The level of predictability in the art;
- (F) The amount of direction provided by the inventor;
- (G) The existence of working examples; and
- (H) The quantity of experimentation needed to make or use the invention based on the content of the disclosure.

The examiner has not applied these factors. Appellants have shown that:

(A) Their claims are as broad as their discovery which is that metal oxides can carry a superconductive current for a  $T_c > 26^\circ \text{K}$ ;

(B) The invention is easily practiced by a person of skill in the art;

(C) The state of the prior art clearly shows how to fabricate materials which can be used to practice appellants' invention;

(D) The level of one of ordinary skill in the art is not high since as stated in the Poole et al. book materials to practice appellants' invention are easily made and all that is needed to practice appellants' claimed invention is to cool the material below the  $T_c$  and to provide a current which will be a superconductive current. It has been well known how to do this since the discovery of superconductivity in 1911. (See page 1 of "Superconductivity" by M. Von Laue)

(E) There is no unpredictability in how to make materials to practice appellants' invention and there is no unpredictability in how to practice applicants' invention. The only unpredictability is which particular metal oxide will have a  $T_c > 26^\circ \text{K}$ . As extensively shown by appellants this is a matter of routine experimentation. The examiner has not denied not rebutted this.;

(F) Appellants have provided extensive direction to make materials to practice their claimed invention. They have included all known principles of ceramic science. Also, as stated in the Poole book these materials are easily made. The examiner has not denied nor

rebutted this. The examiner has made no comment on the amount of direction provided by the appellants;

(G) Appellants have provided sufficient working examples and examples of metal oxides that have  $T_c > 26^\circ\text{K}$  for a person of skill in the art to fabricate materials that can be used to practice appellants' claimed invention; and

(H) Appellants have shown that the quantity of experimentation needed to make samples to use the invention based on the content of the disclosure in the specification is routine experimentation.

The MPEP SECTION---2164.01(a) further states:

The fact that experimentation may be complex does not necessarily make it undue, if the art typically engages in such experimentation. In re Certain Limited-Charge Cell Culture Microcarriers, 221 USPQ 1165, 1174 (Int'l Trade Comm'n 1983), aff'd. sub nom., Massachusetts Institute of Technology v. A.B. Fortia, 774 F.2d 1104, 227 USPQ 428 (Fed. Cir. 1985).

See also In re Wands, 858 F.2d at 737, 8 USPQ2d at 1404. The test of enablement is not whether any experimentation is necessary, but whether, if experimentation is necessary, it is undue. In re Angstadt, 537 F.2d 498, 504, 190 USPQ 214, 219 (CCPA 1976). MPEP 2164

There is no statement by the examiner nor any evidence in the record that the experimentation to make materials to practice appellants' claimed invention

is complex or undue. But it is clear that even if the experimentation was complex to make samples to practice appellants' claimed invention it would not render appellants' claims not enabled since the art typically engages in the type of experimentation taught by appellants to make samples to practice their claimed invention.

The facts of *In re Wands* have similarity to the facts of the present application under appeal. The Court at 8 USPQ2d 1406 held that:

The nature of monoclonal antibody technology is that it involves screening hybridomas to determine which ones secrete antibody with desired characteristics. Practitioners of this art are prepared to screen negative hybridomas in order to find one that makes the desired antibody.

Correspondingly appellants have shown that the nature of high  $T_c$  technology is that it involves preparing samples to determine which ones have  $T_c > 26^\circ\text{K}$  - the desired characteristic. Practitioners of this art are prepared to prepare samples in order to find one that have the desired  $T_c$ . Nothing more is required under *In re Wands*.

Appellants have shown that their specification is enabling with respect to the claims at issue and that there is considerable direction and guidance in the

specification; with respect to appellants' claimed invention there was a high level of skill in the art to fabricate samples at the time the application was filed; and all of the methods needed to practice the invention were well known. Thus appellants have shown that after considering all the factors related to the enablement issue, it would not require undue experimentation to obtain the materials needed to practice the claimed invention. The examiner has not denied nor rebutted this.

A conclusion of lack of enablement means that, based on the evidence regarding each of the above factors, the specification, at the time the application was filed, would not have taught one skilled in the art how to make and/or use the full scope of the claimed invention without undue experimentation. In re Wright, 999 F.2d 1557, 1562, 27 USPQ2d 1510, 1513 (Fed. Cir. 1993). It is the examiner's burden to show this and the examiner has clearly not done so.

The breadth of the claims was a factor considered in Amgen v. Chugai Pharmaceutical Co., 927 F.2d 1200, 18 USPQ2d 1016 (Fed. Cir.), cert. denied, 502 U.S. 856 (1991). In the Amgen case, the patent claims were directed to a purified DNA sequence encoding polypeptides which are analogs of erythropoietin (EPO). The Court stated that:

Amgen has not enabled preparation of DNA sequences sufficient to support its all-encompassing claims. . . . [D]espite extensive statements in the specification concerning all the analogs of the



EPO gene that can be made, there is little enabling disclosure of particular analogs and how to make them. Details for preparing only a few EPO analog genes are disclosed. . . . This disclosure might well justify a generic claim encompassing these and similar analogs, but it represents inadequate support for Amgen's desire to claim all EPO gene analogs. There may be many other genetic sequences that code for EPO-type products. Amgen has told how to make and use only a few of them and is therefore not entitled to claim all of them. 927 F.2d at 1213-14, 18 USPQ2d at 1027.

In the present application appellants have provided a teaching (and proof thereof) of how to make all known high  $T_c$  materials useful to practice their claimed invention. As the Amgen court states this type of disclosure justifies a generic claim. As the *In re Angstadt* court states the disclosure does not have to provide examples of all species within appellants' claims where it is within the skill of the art to make them. There is no evidence to the contrary.

The examiner states "[t]he appellants argue that their own examples do not support the determination of non-enabling scope of the invention. Nevertheless, the record is viewed as a whole. If the applicants could not show superconductivity with a  $T_c > 26^\circ\text{K}$  for certain compositions falling within the scope of the present claims, it is unclear how someone else skilled in the art would have been enabled to do so at the time the invention was made." The examiner avoids the essential issues. Even though appellants' claims do not cover inoperable species, *In re Angstadt* clearly permits a claim to include

inoperable species where to determine which species works does not require undue experimentation. The examiner has not presented any substantial evidence that undue experimentation is required to practice appellants' claim. This is the examiner's burden. On the other hand, appellants have presented five affidavits of experts, the book of Poole and the article of Rao all of which agree that once a person of skill in the art knows of appellants' invention, it is straight forward to fabricate other sample. Also, in response to the examiner's inquiry, "if the applicants could not show superconductivity with a  $T_c > 26^\circ\text{K}$  for certain compositions falling within the scope of the present claims, it is unclear how someone else skilled in the art would have been enabled to do so at the time the invention was made", it is clear that a person of skill in the art would have been enabled by routine experimentation following applicants teaching to determine other samples with  $T_c > 26^\circ\text{K}$ . This is all that is required, and there is no evidence in the record to the contrary.

In the prosecution and the brief, appellants have noted that the examiner has taken a contrary view to appellants' five affiants each of whom has qualified himself as an expert in the field of ceramic technology and in superconductivity. Also, the examiners' argument for nonenablement is primarily based on the examiner "**deeming**" the rejected claims nonenabled based in the unsupported assertion that the art of high  $T_c$  is unpredictable and not theoretically understood, that is, the examiner's opinion or belief that the claims are not enabled. In the prosecution and the brief appellants requested the examiner to

submit an affidavit to qualify himself as an expert to conclusorily "**deem**" the rejected claims nonenabled and to substantiate the unsupported assertions. The examiner has not submitted an affidavit. The examiner's opinions should therefore be stricken from the record. 37 CFR 104(d)(2) states "[w]hen a rejection in an application is based on facts within the personal knowledge of an employee of the office ... the reference must be supported when called for by the applicants, by an affidavit of such employee." (Emphasis Added)

The examiner further states:

The appellants argue that the "Examiner has provided no substantial evidence to support this assertion (of non-enabling scope of the invention). It is respectfully requested that the Examiner support (his) assertion with factual evidence and not unsupported statements." Nevertheless, the determination of non-enabling scope is maintained for the reasons of record.

Appellants note the examiner has not responded to appellant request that the examiner support his view on nonenablement with an affidavit of facts rather than unqualified conclusory statements.

The examiner further states:

The appellants argue that the "standard of enablement for a method of use is not the same as the standard of enablement for a composition of matter" and that their claimed invention is enabling because it is directed to a method of use rather than a composition. Basis is not seen for that argument, to the extent that it is understood.

Applicants discovered that metal oxides had  $T_c > 26^\circ\text{K}$ . This was not known prior to applicants' discovery. Once this is realized, the only enablement required for appellants' claims are to cool a metal oxide below the  $T_c$  and to provide a superconducting current. It is not necessary for applicants to provide a detailed method of making every composition which can be used within the scope of their claims. Applicants' claims are not directed to the composition of matter. They are directed only to the use of the metal oxide as a superconductor with a  $T_c > 26^\circ\text{K}$ , that is, as a circuit element in operation. It was within the skill of the art to fabricate metal oxides using the appellants teaching and test them for a  $T_c > 26^\circ\text{K}$  using techniques well known prior to appellants filing date.

Appellants agree that process of use claims are subject to the statutory provisions of 35 U.S.C. 112, first paragraph. However, those provisions are directed to the claimed process of use invention and not to a composition of matter claim. It is not relevant how a composition, which can be used to practice appellants' claims, is made since the invention is how the composition is used.

Thus the type of enablement is different. For example, if a circuit containing a resistor is claimed, the applicant does not have to teach all known methods to fabricate the resistor and the claim will read on circuits including resistors made by methods discovered after the filing date of the application. Here appellants are claiming a high  $T_c$  superconductor (a type of resistor) that carries a current below a temperature of  $T_c > 26^\circ\text{K}$ . This is a circuit element in operation.

The appellants asserted in the brief and in the prosecution that the examiner has not shown by evidence not contained within appellants' teaching that the art of high  $T_c$  superconductors is unpredictable. In response the examiner states "[t]o the extent that the same assertion is understood, the rejection is maintained for the reasons of record." Applicants' statement is very clear. The examiner is trying to avoid the issue since examiner has not shown by evidence not contained within applicants' teaching that the art of high  $T_c$  superconductors is unpredictable. The examiner has merely "**deemed**" it to be so.

Appellants have extensively referred to "Copper Oxide Superconductors" by Charles P. Poole, Jr., et al., (hereinafter, "the Poole book" or "the Poole article") as supporting their position that higher temperature superconductors were not that difficult to make after their original discovery. This is because methods of making metal oxides which could be used to practice appellants' claimed invention were well known prior to applicants discovery that metal

oxides had a  $T_c > 26^\circ\text{K}$ . In response the examiner states "Initially, however, it should be noted that the Poole article was published after the priority date presently claimed". It is not relevant that the Poole article was published after the priority date since it is clear evidence that only routine experimentation was needed to practice appellants' claimed invention and there is no indication that anything more than appellants' teaching is needed. The examiner further comments on the Poole book stating, "[a]s such, it does not provide evidence of the state of the art at the time the presently claimed invention was made". As noted in the brief, Poole clearly states that the materials that can be used within the scope of applicants claims were easily made. And as stated above the examiner has acknowledged that the fabrication techniques were well known prior to appellants' invention. Poole states that is why so much work was done in so short a period of time. This is clear and convincing evidence that persons of skill in the art were fully enabled by applicants teaching to practice applicants' claimed invention. It is not necessary for appellants to show that the data was generated prior to appellants' filing date. The examiner has not stated, nor is there any evidence presented by the examiner, nor is there any indication in the Poole book that anything more than what appellants taught was necessary to practice appellants' claimed invention. It is only necessary that persons of skill in the art can practice applicants claimed invention from appellants' teaching without undue experimentation. As stated in *In re Angstadt* there is no requirement of no experimentation to practice the claimed invention which is the standard the examiner is apparently applying.

The examiner further states:

Moreover, the present claims are directed to processes of using metal oxide superconductors, not processes of making them. Even if the Poole article provided direct evidence of the state of the art at the time the invention was made, which it apparently does not, that evidence still does not pertain to the issue at hand, namely, the process of using metal oxide superconductors to conduct electricity under superconducting conditions.

The Poole article clearly does not pertain to the process of using metal oxide superconductors to conduct electricity under superconducting conditions prior to appellants' invention since this is appellants' discovery and their invention. The Poole article clearly shows that once appellants revealed their discovery, it was easy to practice appellants' invention and to fabricate other materials to practice appellants' claimed invention. It is not relevant that the Poole article is after the date of appellants' patent application since there is no indication in Poole that anything more than what appellants have taught was used to create the easily created high  $T_c$  materials referred to by Poole. The Poole article clearly shows how these easily made materials can be used to practice appellants' claimed invention. The Poole book is directed to metal oxide materials carrying a superconducting current at  $T_c > 26^\circ\text{K}$  which can be

used in a variety of circuit configurations. Chapter 10 pp . 196-218 of the Poole book is directed to the process of using metal oxide superconductors to conduct electricity under superconducting conditions. The first paragraph of Chapter 10 states:

The principal applications of superconductors are based upon their ability to carry electric current without any loss, and therefore it is important to understand their transport properties. This chapter begins with a discussion of resistivity and critical current flow in the absence of externally applied fields. This is followed by a discussion of several techniques involving applied fields and thermal effects. The chapter concludes with sections on tunneling and the Josephson effect.

Applicants acknowledge the Preface of the Poole Article states in part at A3:" The field of high-temperature superconductivity is still evolving ..." And applicants agree with the examiner that "the field of high-temperature superconductivity continued to grow, on the basis of on-going basic research, after the Bednorz and Meuller article was published." The automobile was discovered prior to 1900 and that field still , more than 100 years latter, continues to grow. The inventor of the automobile would have been able to claim an "automatically moving carriage under the power of an engine" which would be dominant to every automobile manufacture today even through the automobile



technology of today was unknown 100 years ago. Notwithstanding such a dominant claim, others could invent more specific improvements as the field continued to grow, on the basis of on-going basic research. That the field of high-temperature superconductivity continued to grow, on the basis of on-going basic research, after the Bednorz and Meuller article was published does not mean that appellants are not entitled to a claim to their discovery event though it may dominate the inventions of others based on subsequent on-going basis research where that ongoing basis research followed appellants' teaching to fabricate, as taught by appellants, other specific materials to use as taught by appellants.

In the first two full paragraphs on page 20 of the answer the examiner incorrectly refers to three affidavits submitted by appellants. Appellants have submitted five affidavits all of which, as noted above, have been considered and entered. The affidavits of Shaw and Duncombe cited numerous text and articles in support of their affidavits. The affidavit of Duncombe provides several hundred pages of experimental data in regards to fabrication of numerous examples of metal oxides to practice appellants' claimed invention.

Appellants disagree that they have only enabled compositions containing an alkaline earth element and a rare earth or Group IIIB element to result in superconductive compounds which may in turn be utilized in the instantly claimed methods. This new ground for rejection necessitates the introduction of

new evidence to show why the examiners statement is incorrect. As noted above, there are numerous examples of high Tc superconductors made using the general principals of ceramic science as taught by appellants that existed prior to appellants' earliest filing date. Some of that data is in the affidavit of Duncombe, the Poole book and the Rao article.

In regards to the affidavits of Tsui, Dinger and Mitzi the examiner states "However, that additional indication also is considered to be a conclusory statement unsupported by particular evidence." To the extent that this statement is true the affidavits of Shaw and Duncombe, the book by Poole and the article by Rao provide particular evidence. In the answer even though these affidavits and the book by Poole have been considered, the examiner has not commented on this particular evidence and the examiner has not stated that this particular evidence does not support appellants' view that their claims are fully enabled.

The examiner restates what is stated in the affidavits and comments:

It is the examiner's maintained position that while general principles of ceramic fabrication were most certainly known prior to the filing date of the instant application, the utilization of such techniques to produce superconductive materials within the scope of the instant claims were not known. The affidavits are not effective to demonstrate enablement at the time the invention was

made. As stated in paper #66, page 8, one may now know of a material that superconducts at more than 26K, but the affidavits do not establish the existence of that knowledge on the filing date of the present application.

The examiner states: " The affidavits are not effective to demonstrate enablement at the time of the invention was made". Appellants disagree that applicants five affidavits do not demonstrate enablement at the time the invention was made. The affidavits clearly state that the knowledge that existed prior to applicants filing date permitted a person of skill in the art to practice appellants' invention as claimed without undue experimentation. The examiner has presented no evidence to the contrary.

It is not necessary for applicants to provide experimental evidence for all materials that come within the scope of applicants' claims. It is only necessary that a person of skill in the art can practice applicants' claimed invention without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. It is the examiner's burden to show that undue experimentation is required. The examiner has not done this. Also, that there may be specific metal oxides having high  $T_c$ , which are not specifically identified in appellants' specification does not mean that appellants are not entitled to a claim generic to such a species where that species can be made without undue experimentation following appellants' teaching. In re Robins 166 USPQ 552,

555, CCPA 1970, Representative samples are not required by the statute and are not an end in themselves. The examiner has not shown that a person of skill in the art must exercise undue experimentation to make such a species. Thus the examiner has failed to meet his burden.

The examiner concedes that "that while general principles of ceramic fabrication were most certainly known prior to the filing date of the instant application, the utilization of such techniques to produce superconductive materials within the scope of the instant claims were not known." The examiner has acknowledged that techniques to fabricate materials for use within the scope of applicants' claims were known prior to appellants' invention. Appellants agree that "the utilization of such techniques to produce superconductive materials within the scope of the instant claims were not known," since this was appellants' invention. If "the utilization of such techniques to produce superconductive materials within the scope of the instant claims" were known prior to applicants' invention, applicants would not be the inventor. Prior to applicants' discovery persons of skill in the art would not make metal oxides to use as a high  $T_c$  superconductor since such use had to await appellants' discovery. Such fabrication techniques have been used to produce metal oxides for use for some other purpose.

The affidavit of Leonard submitted December 15, 1998 shows that 5,689 articles reference appellants' article. The examiner apparently wants to limit

appellants' claims to their specific embodiments when the record as a whole clearly shows that all known high Tc materials can be made according to appellants' teaching. If the appellants are limited, as the examiner would have them limited, they should not have revealed their discovery and instead spent the rest of their life, in secret, experimenting to generate these 5,689 experimental efforts, according to their original teaching, so that they could get generic claims to their original discovery.

For the reasons given above and in the brief appellants request the board to reverse the examiner's rejection of claims under 35 USC 112, first paragraph.

### ***35 USC 112, Second Paragraph Rejections***

With respect to the remaining claims rejected under 35 U.S.C. 112, second paragraph, the examiner has not rebutted appellant's remarks appearing at pages 102-113 of the Substitute Brief. In response to appellants' arguments that the terms "rare-earth like", " perovskite-like", "layer-type" and "perovskite-type" are definite, the examiner states "those arguments are not found to be persuasive," but the examiner gives no reasons for this view.

At page 21 of the answer, the examiner comments in regard to the claims rejected under 35 UCS 112, second paragraph, the examiner states that "[n]ote the Examiner declines to comment on appellants remarks regarding the

after-final submissions which have not been entered or considered by the examiner." These unentered after final submissions provide evidence that the terminology "perovskite-like", "perovskite-type", and "rare-earth-like" were understood by persons of skill in the art prior to appellants' filing date. This evidence is in addition to evidence previously submitted to show that these terms were well understood in the art. Thus this new evidence is not directed to any new issues but is additional evidence on the same issue. Prior to the Final Action the undersigned attorney requested the examiner to specify what information was needed to convince the examiner that these terms were well understood in the art. The examiner did not provide any guidance to appellants. Thus a trial and error approach was used to see if what was submitted was sufficient to convince the examiner. The examiner again in the Final Action indicated he was not convinced and appellants submitted additional evidence in the after final submissions. Some of the additional evidence is issued US patents having claims containing the identical terminology which the examiner finds indefinite. Other evidence is issued US patents using similar terminology in issued claims indicates that the use of such terminology in US patent claims is standard USPTO practice.

The examiner states:

Each patent application is considered on its own merits. In some contexts it may have been clear in the art to use the term "like",

such as when the "like" term is sufficiently defined. In the present case, however, the terms "rare-earth like" and " perovskite-like" are unclear.

**The examiner would not comment on the after final submissions which bring to the attention of the examiner standard patent office practice which the patent examiner should know.** There are many issued patents having claims including terminology "-type", "-like" and similar combination terms. The examiner's refusal to give reasons for rejecting applicants' use of this terminology while there are many issued patents using this terminology in the claims is "arbitrary and capricious". The examiner must give reasons. It is not sufficient to say "Each patent application is considered on its own merits" without giving reasons as to what the merits are in the present application which render these terms indefinite while not indefinite in the claims of issued patents.

Appellant's published their publication in Z. Phys. B - Condensed Matter 64 (1986) 189-193 (Sept. 1986) which is incorporated by reference in the present specification at page 6, lines 7-10. (This article is referred to here in as a appellants' article.) Appellants filed the first application in the lineage for the present application on May 22, 1987. To the extent that the terminology "perovskite-tpye", "perovskite-like", etc. were not know prior to applicants discovery, it was placed into the vernacular of persons of skill in the art in the approximately eight months between the publication of appellant s' article the

earliest filing date of the present application . Appellants' article was published in a highly regarded physics journal. The referees for the article apparently understood what appellants meant by this terminology. The appellants were awarded a Nobel Prize based on this article. The Nobel committee apparently understood what appellants were referring to. Appellants' article at page 189, fourth line of the abstract, refers to "a perovskite-like mixed-valent copper compound"; at page 189, lines 14-15 of the right column, refers to "perovskite-type or related metallic oxides"; at page 192, line 12 of the left column, refers to "layer-like phases"; and the 8th line of the conclusion at page 192 refers to "a metallic perovskite-type layer-like structure". As stated in the brief at pages 106-107 the book by Poole uses this terminology attributing it to applicants article. Chapter VI, Section D, of the Poole Book is entitled "Pervoskite-type Superconducting Structures" pp. 78-81. It is thus clear that the objected to terminology is understood by persons of skill in the art as of the earliest filing date of the present application. Moreover, as shown in the brief 102 issued United States Patents uses the terminology "pervoskite like", two of which use this term in the claims. It is thus accepted USPTO practice to accept this term as definite. Also, as shown in the brief there are many issued patents using combinations of "-type" and "-like" with claims. Thus it is accepted USPTO practice to accept such terminology as definite.



Moreover, in the brief at pages 7-20, appellants extensively discuss the terminology of the present application which incorporates by reference appellants' article.

Moreover, the affidavits of Duncombe and Shaw refer to a number of articles and texts on the general principles of ceramic science. One of these texts is "Structures, Properties and Preparation of Perovskite-type Compounds", F. S. Galasso (1969). This book was published about eighteen years before appellants' filing date. A copy of the complete text of this book was provided with the affidavits. The examiner does not comment on why a person of skill in the art would not know what a perovskite-type compound was in view of this book and the teaching of applicants' article.

At page 105 of the brief appellants note that in Attachment A of their response of December 11, 1998, there are listed 68 United States Patents using the terminology "rare earth like" or rare earth and the like" and in Attachment B of this response there are listed 4 United States Patents with the term "rare earth like" or similar term in the claims. The examiner has not commented on why this term is not understood by a person of skill in the art in view of the use of this term in the specification and claims of issued United States Patents. In the brief appellants refer to numerous articles using the terminology "rare-earth-like" published before appellants filing date. The examiner has not commented on this. Appellants explain the meaning of "rare-earth-like" at page 7, lines 8-25,

"[a] rare earth-like element (sometimes termed a near rare earth element) is one whose properties make it essentially a rare earth element ...".

It is thus clear that the meaning of "perovskite-type", "perovskite-like" and "rare-earth-like" are apparent from applicants teaching and the prior art, and that it is accepted USPTO practice to use such terminology in the claims. The examiner has not commented on nor rebutted appellants arguments. The examiner has merely stated that there terms are indefinite without further comment.

For reasons given above and in the brief, appellants request the Board to reverse the examiners rejection of claims under 35 USC 112, second paragraph.

### CONCLUSION

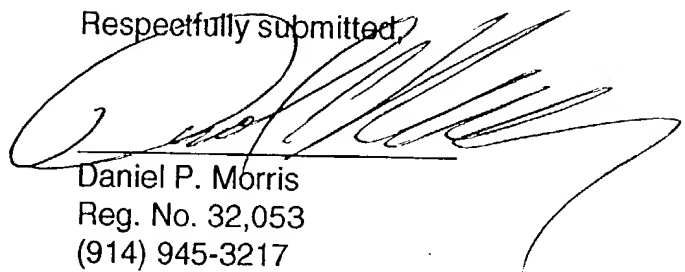
In view of the argument herein and in the brief, Applicants request the Board:

1. reverse the determination that claims 24-26, 86-90, 96-135 and 137-177 are not supported by the priority document;
3. reverse the rejection of claims 24-26, 88-90, 96-102, 109-113, 129-131, 134, 135, 139-142, 145, 149-151, 158, 159, 164-166, 169-170 and 174-177 as not enabled under 35 USC 112, first paragraph; and

4. reverse the rejection of claims 86, 87, 96-108, 112, 113, 117, 118, 122, 123, 127, 128 and 147 indefinite under 35 USC 112 second paragraph.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

Respectfully submitted,

A handwritten signature in black ink, appearing to read 'Daniel P. Morris', is written over a horizontal line. The signature is stylized with a large initial 'D' and a long, sweeping tail.

Daniel P. Morris  
Reg. No. 32,053  
(914) 945-3217

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598

# Attachment A

# THEORY OF SUPERCONDUCTIVITY

By

**M. von LAUE**

Kaiser-Wilhelm-Institut für physikalische und Elektro-Chemie  
Berlin—Dahlem

Translated by

**LOTHAR MEYER**

University of Chicago, Chicago, Illinois

and

**WILLIAM BAND**

The State College of Washington, Pullman, Washington



ACADEMIC PRESS INC., PUBLISHERS

New York, 1952

All Rights Reserved

No part of this book may be reproduced in any form, by photostat, microfilm, or any other means, without written permission from the publishers.

TRANSLATION COMPLETED 1949

Library of Congress Catalog Card Number: 52-7310

## Preface

The aim of this book is to bring our picture of superconductivity into sharper focus by extending Maxwell's electrodynamics along lines first suggested in 1935 by Fritz and Heinz London. This extension will be carried just so far as it succeeds in accounting for known facts, and the reader will see for himself how extensive an area this covers. Beyond this, still exist a number of unexplained facts, which will be ignored. We recall that Clerk Maxwell's electromagnetic theory at first ignored the well known dispersion of the refractive index and that Heinrich Hertz's theory of the electrodynamics of moving bodies ignored the Fresnel drag phenomenon; also, early thermodynamics and gas theory were based on the simple equation of state  $PV = RT$ , although it was known that no actual gas obeyed this equation exactly. After all, theory can approach the truth only by successive approximations.

We have a suspicion that experimental evidence has been insufficient to establish many of these unexplained observations. The ideal solid body, for instance, is a single crystal; but most experiments on superconductivity have been performed with polycrystalline materials, whereas even the best obtainable single crystals, if of useful size, are mosaics of small crystals at whose boundaries the lattice is discontinuous. Hysteresis phenomena are nearly always observed in the transitions between normal states and superconducting states; but we know that at low temperatures, particularly in solid bodies, other relaxation effects may also arise that would completely obscure the theoretical equilibrium between two phases.

Finally many of the unexplained observations have been encountered only a few times, perhaps only once, so that confirmation under varied conditions seems necessary before we are unduly concerned about them.

The phenomenon of superconductivity was discovered in 1911. In spite of this fact, the subject is still only in its initial stages. Should the present theory prove to be true, it will have accomplished for the superconductor what the original Maxwell theory did for the normal conductor and the nonconductor. It does not aim to do more.

In none of its different forms does the atomic theory of superconductivity seem to us to be so far developed that we would wish to include it in this book. It is, however, fairly certain that the persistent current in a superconducting ring is the analog to the atomic persistent currents assumed by the Bohr model to be present inside atoms and molecules. In both cases we are dealing with typical quantum effects which remained unintelligible in classical physics. It seems to me that the main interest for physics in the study of superconductivity lies precisely in this unequivocal experimental proof of the existence of such quantum currents. In any case this book will show how these currents can be fitted into the Maxwell theory.

Recently the first volume of Superfluids by Fritz London was published. His book has partly the same aim as ours, but often uses a different approach. Our *Theory of Superconductivity* actually goes further by including tensor and non-linear generalizations of the theory. There are certain indications that such generalizations are necessary although the final decision depends on future experiments. I believe that this presentation of the theory may serve at least as a stimulus for these experiments: such a suggestion was made by J. Geiss, *Ann. d. Phys.* (6), 9, 40, 1951.

MAX von LAUE

December, 1951

## Table of Contents

PREFACE . . . . .	Page	v
SYMBOLS . . . . .	viii	
CHAPTER		
1. Fundamental Facts . . . . .	1	
2. Current Distribution between Superconductors in Parallel . . . . .	8	
3. Fundamental Equations of the Maxwell-London Theory . . . . .	12	
4. Space Charges in Superconductors . . . . .	19	
5. The Conservation of Energy . . . . .	20	
6. The Telegrapher's Equation for Superconductors with Cubic Crystal Structure . . . . .	22	
7. Stationary Fields . . . . .	24	
8. The Current Flowing in a Wire . . . . .	35	
9. The Current Flowing in a Hollow Cylinder . . . . .	44	
10. The Cylinder in a Homogeneous Magnetic Field . . . . .	48	
11. The Sphere in a Homogeneous Magnetic Field . . . . .	55	
12. Persistent Currents . . . . .	61	
13. The Maxwell and London Stresses . . . . .	75	
14. The Electrodynamical Potential . . . . .	84	
15. Electric Waves in Superconductors with Cubic Crystal Structure . . . . .	91	
16. The High-Frequency Resistance of Superconductors . . . . .	94	
17. Thermodynamics of the Transition between Normal and Superconducting Phases . . . . .	103	
18. The Critical Magnetic Field for Thin Superconductors . . . . .	112	
19. The Intermediate State . . . . .	119	
20. A Nonlinear Extension of the Theory . . . . .	126	
APPENDIX . . . . .	137	
INDEX . . . . .	139	

All Rights Reserved

No part of this book may be reproduced in any form, by photostat, microfilm, or any other means, without written permission from the publishers.

TRANSLATION COMPLETED 1949

Library of Congress Catalog Card Number: 52-7310

## Preface

The aim of this book is to bring our picture of superconductivity into sharper focus by extending Maxwell's electrodynamics along lines first suggested in 1935 by Fritz and Heinz London. This extension will be carried just so far as it succeeds in accounting for known facts, and the reader will see for himself how extensive an area this covers. Beyond this, still exist a number of unexplained facts, which will be ignored. We recall that Clerk Maxwell's electromagnetic theory at first ignored the well known dispersion of the refractive index and that Heinrich Hertz's theory of the electrodynamics of moving bodies ignored the Fresnel drag phenomenon; also, early thermodynamics and gas theory were based on the simple equation of state  $PV = RT$ , although it was known that no actual gas obeyed this equation exactly. After all, theory can approach the truth only by successive approximations.

We have a suspicion that experimental evidence has been insufficient to establish many of these unexplained observations. The ideal solid body, for instance, is a single crystal; but most experiments on superconductivity have been performed with polycrystalline materials, whereas even the best obtainable single crystals, if of useful size, are mosaics of small crystals at whose boundaries the lattice is discontinuous. Hysteresis phenomena are nearly always observed in the transitions between normal states and superconducting states; but we know that at low temperatures, particularly in solid bodies, other relaxation effects may also arise that would completely obscure the theoretical equilibrium between two phases.

Finally many of the unexplained observations have been encountered only a few times, perhaps only once, so that confirmation under varied conditions seems necessary before we are unduly concerned about them.

The phenomenon of superconductivity was discovered in 1911. In spite of this fact, the subject is still only in its initial stages. Should the present theory prove to be true, it will have accomplished for the superconductor what the original Maxwell theory did for the normal conductor and the nonconductor. It does not aim to do more.

In none of its different forms does the atomic theory of superconductivity seem to us to be so far developed that we would wish to include it in this book. It is, however, fairly certain that the persistent current in a superconducting ring is the analog to the atomic persistent currents assumed by the Bohr model to be present inside atoms and molecules. In both cases we are dealing with typical quantum effects which remained unintelligible in classical physics. It seems to me that the main interest for physics in the study of superconductivity lies precisely in this unequivocal experimental proof of the existence of such quantum currents. In any case this book will show how these currents can be fitted into the Maxwell theory.



Recently the first volume of Superfluids by Fritz London was published. His book has partly the same aim as ours, but often uses a different approach. Our *Theory of Superconductivity* actually goes further by including tensor and non-linear generalizations of the theory. There are certain indications that such generalizations are necessary although the final decision depends on future experiments. I believe that this presentation of the theory may serve at least as a stimulus for these experiments: such a suggestion was made by J. Geiss, *Ann. d. Phys.* (6), 9, 40, 1951.

MAX von LAUE

December, 1951

## Table of Contents

PREFACE . . . . .	Page v
SYMBOLS . . . . .	viii
CHAPTER	
1. Fundamental Facts . . . . .	1
2. Current Distribution between Superconductors in Parallel . . . . .	8
3. Fundamental Equations of the Maxwell-London Theory . . . . .	12
4. Space Charges in Superconductors . . . . .	19
5. The Conservation of Energy . . . . .	20
6. The Telegrapher's Equation for Superconductors with Cubic Crystal Structure . . . . .	22
7. Stationary Fields . . . . .	24
8. The Current Flowing in a Wire . . . . .	35
9. The Current Flowing in a Hollow Cylinder . . . . .	44
10. The Cylinder in a Homogeneous Magnetic Field . . . . .	48
11. The Sphere in a Homogeneous Magnetic Field . . . . .	55
12. Persistent Currents . . . . .	61
13. The Maxwell and London Stresses . . . . .	75
14. The Electrodynamical Potential . . . . .	84
15. Electric Waves in Superconductors with Cubic Crystal Structure . . . . .	91
16. The High-Frequency Resistance of Superconductors . . . . .	94
17. Thermodynamics of the Transition between Normal and Superconducting Phases . . . . .	103
18. The Critical Magnetic Field for Thin Superconductors . . . . .	112
19. The Intermediate State . . . . .	119
20. A Nonlinear Extension of the Theory . . . . .	126
APPENDIX . . . . .	137
INDEX . . . . .	139

## SYMBOLS

A	vector potential	$H^0$	external homogeneous magnetic field
$a_p$	undetermined constants, $p = 1, 2, \dots$	$H_c$	critical magnetic field
$a$	a numerical ratio	$H_e, H_c$	internal and external values of $\mathbf{H}$
$\alpha_p$	undetermined constants, $p = 1, 2, \dots$	$H_0(x)$	Hankel's function of $x$ , first kind zero order
B	magnetic induction	$H_1(x)$	Hankel's function of $x$ , first kind first order
$\beta$	reciprocal penetration depth	$I$	electric current in a line or current in a surface
c	velocity of light	$i$	electric current density vector
$C_m$	closed curves $m = 1, 2, \dots$	$i_\alpha$	components of $\mathbf{i}$ , $\alpha = 1, 2, 3$
$c_N, c_S$	specific heats per mol of normal and superconducting phases	$i_1, i_2, i_3$	$i_1, i_2, i_3$ , components of $\mathbf{i}$ , cartesian or polar
$\kappa$	an undetermined multiplier	$j^0$	ohmic current density vector
D	electric displacement	$j^1$	supercurrent density vector
$d$	distance	$j_m$	maximum current density vector
$\delta A$	work done in virtual displacement	$j_n$	current density normal to a given surface element
$\partial A$	work done in material displacement	$j_s$	surface density of current
$\delta F$	change in free energy in virtual displacement	$(\mathbf{i} \cdot \mathbf{G})$	scalar product of $\mathbf{i}$ and $\mathbf{G}$
$\delta n$	virtual displacement of a surface element	$i$	square root of minus one
$d\sigma$	surface element	$J_n(x)$	Bessel functions, $n = 0, 1, 2$
$ds$	line element	k	complex wave number
$d\tau$	volume element	$k_n$	complex wave number for normal conductor
$\partial u$	material displacement	$\mathbf{K}_n$ or $\mathbf{K}_y$	total force on a surface element due to electromagnetic stress
$\partial V$	potential energy change due to material displacement	$\mathbf{K}$	force per unit volume in matter due to Maxwell-London stresses
E	electric field intensity	$L$	a length
$E_a$	electric field components, $a = 1, 2, 3$	$\lambda$	superconductivity constant
$E$	total energy	$\lambda_{ab}$	superconductivity tensor $a, b = 1, 2, 3$
$E_0$	amplitude of E waves	M	intensity of permanent magnetisation
$[\mathbf{E} \times \mathbf{H}]$	vector product of $\mathbf{E}$ and $\mathbf{H}$	$\mu$	magnetic permeability
$\epsilon$	dielectric constant	N	number of superconducting electrons per cubic centimeter
$\epsilon$	free energy	n	unit normal vector
$N, /s$	free energy per mol of normal and superconducting phases	$n_i, n_s$	unit normal vector directed inwards or outwards
$\rho_n, \tau_1$	force per unit area due to Maxwell stresses	$\nu$	frequency (numerical)
$\tau_1$	free energy of supercurrent	$\mathbf{P}_n$	force on surface due to London stresses
i	electromagnetic momentum associated with the supercurrent	$p_{ab}$	coefficients of induction $a, b = 1, 2, \dots$
$i_a$	components of $\mathbf{G}$ , $a = 1, 2, 3$	$p^{ss}$	self-induction for superconductors
.	a numerical factor	$p^{se}$	mutual induction between super- and normal conductor
l	magnetic field intensity vector	$\varphi$	azimuthal angle
$\mathbf{l}_a$	components of $\mathbf{H}$ , $a = 1, 2, 3$	$\phi$	imaginary part of a complex function
		$\Phi$	electrostatic or magnetostatic potential
		$\psi$	real part of a complex function
		$\bar{\psi}$	superconduction scalar potential
		Q	quantity of heat
		Q	cross cut in $n$ -ply connected region
		Q	rate of flow of energy in radiation field

x

$R_e$  real part of complex function  
 $R$  a radius  
 $R_i, R_e$  internal and external radii  
 $r, \theta, \varphi$  polar coordinates  
 $\rho$  charge density  
 $\rho^o$  charge density for ohmic current carriers  
 $\rho^s$  charge density for supercurrent carriers

$S_N, S_S$  entropy per mol in normal and superconducting phases  
 $S$  linear dimensions of a surface  
 $S_C$  „period“ of a multiple valued function on a curve  $C$   
 $\sigma$  equal to the flux of induction thru the loop  $C$   
 $\sigma$  electric conductivity  
 $\sigma_{ab}$  electric conductivity tensor  $a, \beta = 1, 2, 3$

$T$  temperature in  $^{\circ}\text{K}$   
 $T_s$  transition temperature for superconductivity  
 $T(E)$  Maxwell stress tensor  
 $T(H)$  Maxwell stress tensor  
 $t$  time  
 $t_a$  numerical constants  $a = 1, 2, \dots$   
 $\tau_a$  latitude angle  
 $\theta_s, \theta_s$  Debye temperatures for normal and superconducting phases  
 $\partial_{\omega^2}$  The London stress tensor in superconductor  $a, \beta = 1, 2, 3$

$\mathcal{I}$  total energy of the field  
 $\mathcal{I}$  real part of complex function  $W$   
 $\mathcal{I}$  a general function of position and time  
 $\mathcal{I}$  volume or potential  
 $\mathcal{I}$  imaginary part of complex function  $W$   
 $\mathcal{I}$  electromotive force

$\mathcal{I}$  resistance  
 $\mathcal{I}$  a complex function  
 $\mathcal{I}$  angular frequency  
 $\mathcal{I}$  differential operator for the telegrapher's equation

$\gamma, z$  cartesian coordinates  
 $x_2, x_3$  cartesian coordinates  
 $\gamma$  a function in the complex plane  
 $\gamma$  permeability  
 $\gamma$  complex impedance  
 $\gamma$  a function in the complex plane  
 $\gamma$  a variable of integration

## CHAPTER 1

### Fundamental Facts

(a) Superconductivity was discovered in 1911 by Kamerlingh-Onnes.<sup>1</sup> He was the first to liquefy helium and so to produce temperatures below 10° K. With this new technique he was able to observe the continued decrease of the electrical resistance of metals with decreasing temperature. With mercury, in contrast to other metals, he was astonished to find that the resistance completely vanished, almost discontinuously, at about 4.2° K (Fig. 1-1). Today superconductivity is known in 18 other metals (see Table 1-1) whereas in others, e. g., gold and bismuth, the conductivity remains normal far below even 1° K. Many alloys and compounds can also become superconducting, in particular the frequently used niobium nitride which has a transition temperature as high as 20° K. However, among these latter substances hysteresis phenomena mentioned in the “Introduction” are so much more strongly evident that in testing the present theory we prefer to employ only the “good” superconductors, i. e., the pure elements.

In the ideal case the resistance vanishes completely and discontinuously at a transition temperature  $T_s$ . Actually the resistance-temperature curve does fall more sharply the more the specimen is like a single crystal and the smaller the measuring current used. Because the drop always occurs in a measurable temperature range, the experimental definition of the transition temperature is to some extent arbitrary. The temperature at which the direct-current resistance reaches one half of the value it had just before the drop is generally given as the transition temperature, because this can be measured accurately. However, a high-frequency investigation to be described in Chap. 16 (f) indicates that the foot of the curve where

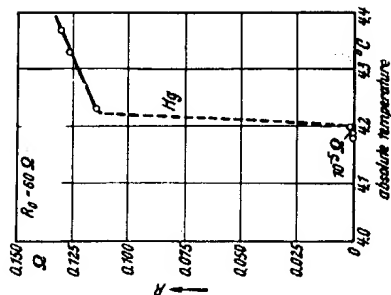


Fig. 1-1. Appearance of superconductivity in mercury according to H. Kamerlingh-Onnes (1911). The ordinate is the resistance  $R$ ;  $R_0$  the resistance of solid mercury extrapolated to 0° C. is 60 ohms.

just before the drop is generally given as the transition temperature, because this can be measured accurately. However, a high-frequency investigation to be described in Chap. 16 (f) indicates that the foot of the curve where

<sup>1</sup>H. Kamerlingh-Onnes, *Commun. Leiden*, 120b, 122b, 124c, (1911).

3

Table 1—1  
Superconducting Elements

Name	Atomic Number	Transition Temperature	Crystallographic System	Crystal Class*
unium	13	1.2 °K	Cubic	$O_h$
anium	22	0.5 °K	Cubic and hexagonal	$O_h$ and $D_{6h}$
adium	23	4.3 °K	Cubic	$O_h$
ic	30	0.9 °K	Hexagonal	$D_{6h}$
ilium	31	1.1 °K	Rhombic	$V_h$
onium	40	0.7 °K	Cubic and hexagonal	$O_h$ and $D_{6h}$
ibium	41	9.2 °K	Cubic	$O_h$
imium	48	0.6 °K	Hexagonal	$D_{6h}$
ium	49	3.4 °K	Tetragonal	$D_{4h}$
thanium	50	3.7 °K	Tetragonal†	$D_{4h}$
anium	57	4.7 °K	Cubic and hexagonal	$O_h$ and $D_{6h}$
tanium	72	0.3 °K	Hexagonal	$D_{6h}$
ium	73	4.4 °K	Cubic	$O_h$
ium	75	0.9 °K	Hexagonal	$D_{6h}$
cury	80	4.2 °K	Rhombohedral	$D_{3d}$
ilium	81	2.4 °K	Cubic and hexagonal	$O_h$ and $D_{6h}$
ium	82	1.2 °K	Cubic	$O_h$
ium	90	1.4 °K	Cubic	$O_h$
ium	92	0.8 °K	Rhombic	$V_h$

The atomic structure does not change during the transition from normal conductor to superconductor, therefore the crystal class does not change either. The classes are defined according to symmetries.

Besides the tetragonal white tin there exists a gray modification with a crystal structure of the diamond type which, however, does not become superconducting.

In order to obtain curves such as in Fig. 1-1, the resistance is calculated at the potential drop along a wire carrying a current. For this purpose the potential leads are soldered to the ends of the wire, in addition to the leads for the current, and are connected to a highly sensitive potentiometer. But if one merely wishes to verify the complete disappearance in resistance below the transition temperature  $T_c$ , experiments with persistent currents, also due to Kamerlingh-Onnes,<sup>2</sup> are far more convincing exact.

b) One possible procedure is to place a ring or short-circuited coil in magnetic field while its temperature is still above  $T_c$ , cool it down until conductivity appears, and then remove it from the field. The induced

I. Kamerlingh-Onnes, *Commun. Leiden*, 140b, 141b, (1914).

electromotive force produces a current in the superconductor which will persist indefinitely unchanged in magnitude as long as superconductivity remains. The ring forms an ideal permanent magnet, and, when placed in an external homogeneous magnetic field, it experiences a torque corresponding to its magnetic moment. Two rings with persistent currents attract or repel each other, depending on their relative orientations, just as for ordinary currents, except that no emf's are needed to maintain them. It does not matter whether the rings are homogeneous or consist of several different superconductors, or whether their temperature is constant in space or time; it is only necessary that no part of the ring shall leave the superconducting state.<sup>3</sup> Should this occur, the current is quenched almost instantaneously. For example, a ring carrying a persistent current may be cut at some point across which a galvanometer has been connected through normally conducting leads. Before the cut is made, the galvanometer will register zero current; but at the instant that the ring is broken, it will show a short current impulse. The energy of the persistent current, for the most part magnetic energy, is then transformed into joule heat in the normally conducting wires.

A necessary condition for the existence of any persistent current is that the superconductor form a doubly connected body or, briefly, a ring, or more generally a multiply connected body. No persistent currents can exist in a simply connected body such as a sphere. Results that apparently contradict this arise because only parts of the specimen, among them doubly or multiply connected parts, may become superconducting, while the rest of the specimen remains either normal or in the intermediate state (see Chap. 12 (g) and 19). An electromagnet using the persistent current has been described by E. Justi.<sup>4</sup>

(c) In contrast to the normal current, which we shall call the ohmic current, the superconducting current (or supercurrent) does not penetrate very far into the specimen. It has been known for a long time that the superconductivity of thin tin films on copper or some other normally conducting metal, even down to a thickness of only  $10^{-4}$  cm, does not differ from the superconductivity of thick tin wires. The contradictory evidence found by Burton<sup>5</sup> using somewhat thinner films is outweighed by the observations of Shalnikov<sup>6</sup> and by those of Appleyard and Misener<sup>7</sup> using lead, tin, and mercury films as thin as  $5 \times 10^{-7}$  cm. These workers found practically the same transition temperatures as in the bulk metals, the small differences observed being within the experimental error.

The first quantitative estimates of the penetration depth of the super- $\pi$  current and its associated magnetic field derived from observational evidence,

<sup>3</sup>It is fairly certain that temperature fluctuations in the water investigated has ever mentioned any such effect.

<sup>4</sup>E. Justi, *Elektrotech. Z.*, **68**, 577 (1942). ✓

<sup>5</sup>E. F. Burton, *Nature*, 183, 459 (1934).

<sup>6</sup>A. Shalnikov, *Nature*, 142, 74 (1938).

<sup>7</sup>T. S. Appleyard and A. D. Misener, *Nature*, **142**, 474 (1938).

were made by the author<sup>8</sup> from the experimental results of Pontius using lead wires<sup>9</sup> (Fig. 18-1). Appleyard, Bristow, and H. London<sup>10</sup> and a year later Shoenberg<sup>11</sup> found the same order of magnitude, namely  $10^{-6}$  cm, using films and spherical drops of mercury. This holds for temperatures within a few tenths of a degree below the transition temperature  $T_c$ . However, if we are within one-tenth of a degree of  $T_c$ , according to the above work of Shoenberg, the penetration depth increases suddenly and appears to become infinitely great at the transition point (see Fig. 11-3). This means that in a certain sense the electrical properties of the superconductor change continuously into those of the normal conductor. The measurements by McLennan, Burton, Pitt and Wilhelm<sup>12</sup> and H. London<sup>13</sup> in the high-frequency resistance of superconductors also fit in with this concept: the resistance to rapid oscillations showed no discontinuity at the transition point, but joined smoothly at  $T_c$  with that of the high-frequency resistance of the normal conductor (Fig. 16-2).

(d) The transition from normal to superconductor does not change the form or the volume of the specimen; its lattice remains the same not only in its symmetry but also in its three lattice constants. This was proved or lead by Kamerlingh-Onnes and Keesom using x-ray analysis.<sup>14</sup> The coefficient of thermal expansion (which incidentally is very small) does not change at the transition. Of special significance is the optical identity of the two phases, because in normal conductors the optical constants are intimately related to the electrical conductivity. The observations of Daunt, Keely, and Mendelssohn,<sup>15</sup> of Hirschlaff,<sup>16</sup> and of Hirsch<sup>17</sup> revealed no difference in the appearance of the metal. One cannot tell by visual observation whether the metal is normal or superconducting.

(e) The relation between superconductivity and magnetic field is of the highest significance. The first steps toward disclosing this relation were made in 1913 by Kamerlingh-Onnes<sup>18</sup> who noticed that at each temperature there existed a critical value  $H_c$  of the magnetic field that could destroy the superconductivity. We can obtain the simplest and earliest results by putting a wire in a longitudinal magnetic field, i. e.,

<sup>8</sup> M. v. Laue, *Ann. Physik*, **82**, 71, 253 (1938).

<sup>9</sup> R. B. Pontius, *Nature*, **189**, 1065 (1937).

<sup>10</sup> T. S. Appleyard, T. R. Bristow, and H. London, *Nature*, **148**, 433 (1939).

<sup>11</sup> D. Shoenberg, *Nature*, **148**, 434 (1939).

<sup>12</sup> E. Laurmann and D. Shoenberg, *Nature*, **160**, 747 (1948).

<sup>13</sup> C. McLennan, A. C. Burton, A. Pitt, and J. O. Wilhelm, *Proc. Roy. Soc. (London)*, **6**, 52 (1932); **188**, 245 (1934).

<sup>14</sup> W. H. Keesom and H. Kamerlingh-Onnes, *Commun. Leiden*, **176**, 522 (1940).

<sup>15</sup> J. G. Daunt, T. C. Keely, and K. Mendelssohn, *Phil. Mag.*, **28**, 264 (1924).

<sup>16</sup> E. Hirschlaff, *Proc. Cambridge Phil. Soc.*, **88**, 140 (1937).

<sup>17</sup> R. Hirsch, *Physik. Z.*, **40**, 592 (1939).

<sup>18</sup> H. Kamerlingh-Onnes, *Commun. Leiden Supplement* **35** (1913).

parallel to the axis of the wire. The dependence of the a-c resistance on the magnetic field  $H$  for this case is shown in Fig. 1-2, while Fig. 1-3 shows the critical value of the magnetic field as a function of temperature for several metals.

Figure 1-4 shows an extrapolation of these curves down to the absolute zero of temperature according to a relation that is empirically confirmed in some cases:

$$H_c = a(T_c^2 - T^2)$$

At  $T = 0$  the tangent of this curve is horizontal, as thermodynamics demands (Chap. 17). The maximum values of  $H_c$  at  $T = 0$  lie between 100 and 1000 oersteds for pure metals and may be much higher for alloys and compounds.

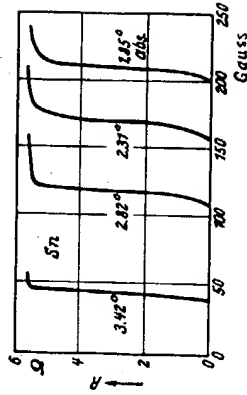


Fig. 1-2. Transition to superconductivity in a longitudinal magnetic field for tin at different temperatures. (After Steiner and Grassmann, *Supraleitung*, Braunschweig, 1937.)

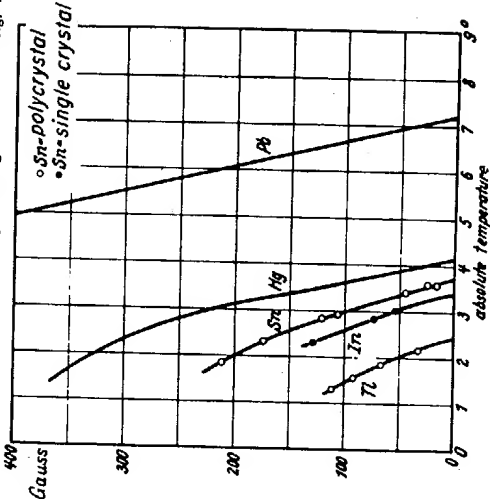


Fig. 1-3. Critical value of the magnetic field  $H_c$  as a function of temperature for different metals. (After Steiner and Grassmann, *Supraleitung*, Braunschweig, 1937.)

A current  $I$  produces at the surface of a straight wire of radius  $R$  a magnetic field  $H$ :

$$H = \frac{I}{2\pi cR} \quad (1-1)$$

n Lorentz units, which we shall generally employ.<sup>19</sup> We should therefore expect to find a critical value  $I_c$  of the current which would destroy superconductivity, and this has been confirmed by observation. According to eq. (1-1) the relation between  $I_c$  and  $H_c$  ought to be

$$I_c = 2\pi cR H_c \quad (1-2)$$

This was first pointed out by Silsbee,<sup>20</sup> and it is therefore called the Silsbee hypothesis. Most measurements do not agree with eq. (1-2), although in one case it has been confirmed by a very careful series of measurements by Shubnikov and Alexejevski.<sup>21</sup> This is one of the weakest points in our understanding of superconductivity; a failure of eq. (1-2) means nothing less than a failure of the fundamental Maxwell relation connecting curl  $\mathbf{H}$  and current density  $\mathbf{i}$ . No one at present credits such a failure, and the theory developed here is based essentially on this equation. It is to be hoped that experimental work will be able to remove this uncertainty.

(f) The earliest theory of superconductivity visualized the superconductor simply a conductor with zero resistance. But on the Maxwell theory this assumption would have an important consequence; the interior of a perfect conductor would be completely shut off electromagnetically from any outside influence. If such a conductor were placed in a static magnetic field, its interior would remain field free, the lines of force, or rather of induction, would diverge in front and converge behind as if going round a body of zero permeability (Fig. 1-5). But the result would be different if one were to put the specimen in an external field while it was still above transition temperature  $T_c$ , and then cool it in the field until the resistance appeared. Above  $T_c$  the lines of force would go through the metal without difficulty because the permeability of the metals under consideration is actually unity so long as they are in the normal state. This theory however asserts that the appearance of superconductivity cannot by itself alter the field. The lines of force would still go through the specimen undeviated. The contrary, Meissner and Ochsenfeld<sup>22</sup> showed in 1933 that the final

<sup>19</sup> If  $I$  is measured in amperes and  $H$  in oersteds  $H = 0.2 I/R$ .

<sup>20</sup> F. B. Silsbee, *J. Washington Acad. Sci.*, **6**, 597 (1916); Pap. Bureau of Standards 307 (1917).

<sup>21</sup> L. W. Shubnikov and N. E. Alexejevski, *Nature*, **138**, 804 (1936).

<sup>22</sup> W. Meissner and R. Ochsenfeld, *Naturwissenschaften*, **21**, 787 (1933).  
W. Meissner, *Physik. Z.*, **35**, 931 (1934).

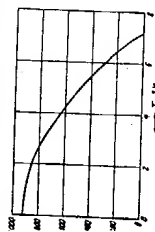


Fig. 1-4. Critical value of magnetic field  $H_c$  as a function of temperature for lead (approximate curve).

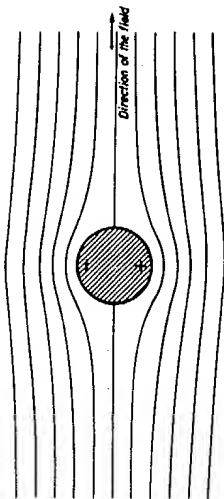


Fig. 1-5. The transverse field near a superconducting circular cylinder. The lines of force are plotted from the equation, in polar coordinates:

$$(r - R^2/r) \sin \theta = C \quad \text{for} \quad C = 0, \quad \pm 1/2 R, \quad \pm R, \quad \pm 3/2 R, \quad \pm 2 R, \quad \pm 5/2 R.$$

+ or - means the supercurrent flows toward or away from the reader respectively.

This fact permits us to interpret the super- and normal conductors as two phases of the same substance, whereas according to the older theory the state inside the superconductor was not determined intrinsically. Under this condition we can now apply thermodynamics to the equilibrium between the normal and the superconducting state (see Chap. 17). The London extension of the Maxwell theory is also based essentially on the expulsion of the field, called the Meissner effect.

(g) The older conception permitted us to calculate the field deformation near a thick superconductor accurately enough when the cooling precedes the application of the field. It showed that the distortion of the lines of force at certain points of the surface increases the field strength (see Fig. 1-5); for a superconducting sphere in a homogeneous field by a maximum factor  $3/2$ ; for a circular cylinder in a transverse field by a factor 2, and for an elliptical cylinder with cross-sectional axes  $a$  and  $b$  by the factor  $(1 + b/a)$  when the field is parallel to the  $a$  axis.

It was thus possible in 1932 — even before the Meissner discovery — for the author<sup>23</sup> to explain the fact that a transverse external field  $1/2 H_c$  was sufficient to quench the superconductivity in a wire. It was also predicted that an elliptical cylinder would show a greater decrease of the apparent

<sup>23</sup> M. V. Laue, *Physik. Z.*, **33**, 793 (1932).

state is in fact identical in the two cases — it does not depend on the previous history. In a singly connected superconductor everything is uniquely determined by its temperature and the apparatus producing the external field: in an  $n$ -ply connected body there is a possibility of  $n - 1$  persistent currents and their magnetic fields whose strengths are optional within certain limits. But in any case the interior of a sufficiently thick superconductor is field free. The field-free state is the only state in such a superconductor.

critical value than a circular cylinder if the field were perpendicular to the greater axis; also for a sphere the apparent critical value would amount to  $(2/3)H_c$  (see Chap. 10 (c) and (d), and Chap. 11). All these predictions were confirmed by an extensive series of measurements by de Haas and co-workers<sup>24 25</sup>. In this work it was also found that the most certain indication of the breakdown of superconductivity was not the reappearance of an ohmic resistance, but the appearance of a magnetic field in the interior of the specimen as detected by means of small bismuth wires placed in cavities in the specimen. The whole specimen does not immediately become normally conducting with the disappearance of superconductivity; instead the "intermediate state" almost always appears, a mechanical mixture of normal and superconducting parts (Chap. 19). As long as the latter form a connected path they take over the conduction of the current exclusively.

(b) Finally our book will discuss thermal measurements, e. g., the heat required in the transition to normal from superconducting states, whenever his takes place in a magnetic field; or the specific heats of the normal and superconductors. But we shall postpone any more detailed discussion of this until Chap. 17 where the thermodynamics will reveal relations between these caloric phenomena and the critical magnetic field.

## CHAPTER 2

### Current Distribution Between Superconductors in Parallel

(a) If between two points of a normally conducting system there are  $n$  branches with resistances  $r_1, r_2, \dots, r_n$ , then the ratios of the direct currents are

$$I_1 : I_2 : \dots : I_n = \frac{1}{r_1} : \frac{1}{r_2} : \dots : \frac{1}{r_n}$$

his rule of Kirchhoff's remains valid when one branch becomes superconducting, e. g.,  $r_n = 0$ . This states that  $I_1 = I_2 = \dots = I_{n-1} = 0$ , i. e., the superconductor short-circuits all the other branches. If we apply an emf such a system consisting of one and the same metal above the transition temperature, then the rule still holds even if we cool the metal until superconductivity appears. The appearance of superconductivity does not change the individual currents if the total current  $\sum_{k=1}^n I_k$  is kept constant. As a matter of fact any (possible) cause for such a change disappears as the mutual inductions between all the currents  $I_k$  vanish.

<sup>24</sup>W. J. de Haas and J. M. Casimir-Jonker, *Physica* 1, 291 (1934).

<sup>25</sup>W. J. de Haas and O. A. Guineau, *Physica* 1, 291 (1934).

<sup>26</sup>W. J. de Haas, A. D. Engelkes, and O. A. Guineau, *Physica* 4, 595 (1937).

If initially all values of  $r_k = 0$ , the Kirchhoff rule cannot be applied at all. The calculation of the current distribution must be based upon the fact that the current is initiated by means of a voltage  $V$ , formed between the junctions, which changes with time and dies out as soon as the currents become stationary, the whole process being described in terms of the laws of induction. In using these laws we have to assume that the inductive coupling between the  $n$  branches is much stronger than their coupling with the leads to the junctions. This condition is fulfilled by inserting coils with considerable mutual inductance in the branches and by having the leads in the form of straight wires which do not come too close to the coils. The magnetic field of the system is then mainly confined to the vicinity of the coils.

Under these conditions the magnetic field strength  $H$  is a linear function of the currents  $I_k$  at every point; the energy density  $\frac{1}{2} H^2$  and also the total magnetic energy

$$\frac{1}{2} \int H^2 dx dy dz = \frac{1}{2} \sum_{k,l} p_{kl} I_k I_l$$

is therefore a quadratic form in  $I_k$ . This form is necessarily positive and definite, i. e., all  $p_{kl}$ , the determinant of the  $p_{kl}$ , as well as all subdeterminants symmetrical with respect to the diagonal, are positive. For  $n = 2$ ,

$$p_{11} > 0, \quad p_{22} > 0, \quad p_{11}p_{22} - p_{12}^2 > 0 \quad (2-1)$$

The  $p_{kl}$  are the coefficients of self induction, the "mixed" terms  $p_{kl}$  are the coefficients of mutual induction.  $p_{kl} = p_{lk}$  identically.

It is possible to derive Maxwell's equations from the principle of least action by considering the electric energy as the potential energy and the magnetic energy as the kinetic energy. If electric currents are flowing, the work  $V \cdot \delta e$  performed by the emf's has to be taken into consideration, where  $\delta e$  is the amount of electricity transported in a given direction by the current  $I$ . Here we have to do with quasi-stationary processes for which the electric energy vanishes compared with the magnetic energy. Under the assumption that the magnetic energy is the only energy depending on the currents, this principle now reads:

$$\delta \left( \frac{1}{2} \sum_{k,l} p_{kl} I_k I_l - V \sum_k e_k \right) dt = 0 \quad (2-2)$$

As  $-I_k = de_k/dt$  is the velocity corresponding to the coordinate  $e_k$ , the corresponding Euler equations are

$$\frac{d}{dt} \left( \sum_l p_{kl} I_l \right) - V = 0 \quad (k = 1, 2, \dots, n) \quad (2-3)$$

and we recognize these as the usual induction equations. They are immediately integrable with respect to time  $t$ , and if all  $I_k$  are zero at  $t = 0$  we obtain

$$\sum_i \dot{p}_{ii} I_i = \int V dt \quad (2-4)$$

is holds for all times, including the final state in which all  $I_k$  have become stationary and  $V = 0$  by eq. (2-5). Unfortunately the quantity  $\int V dt$  is not determined by the experiment, but only the current  $I = \sum_k I_k$  in the steady state, namely by a galvanometer in the leads. However, together with the equation  $I = \sum_k I_k$ , eq. 2-4 forms  $n + 1$  linear relations between  $n + 1$  unknowns  $I_1, I_2, \dots, I_n$  and  $\int V dt$ . For the special case  $n = 2$ , 2-4 gives

$$\dot{p}_{11} I_1 + \dot{p}_{12} I_2 = \dot{p}_{21} I_1 + \dot{p}_{22} I_2 = \int V dt \quad (2-5)$$

erefore because  $I_1 + I_2 = I$  we have

$$I_1 = \frac{\dot{p}_{22} - \dot{p}_{12}}{\dot{p}_{11} + \dot{p}_{22} - 2\dot{p}_{12}} I \quad I_2 = \frac{\dot{p}_{11} - \dot{p}_{12}}{\dot{p}_{11} + \dot{p}_{22} - 2\dot{p}_{12}} I \quad (2-6)$$

regard  $I$  as positive; a positive  $I_k$  means that this current flows in the direction as  $I$ ; a negative  $I_k$  means that it has the opposite direction. According to eq. 2-1 and because the geometric mean of two positive entities lies below the arithmetic mean:

$$|\dot{p}_{12}| < \sqrt{\dot{p}_{11} \dot{p}_{22}} < \frac{1}{2} (\dot{p}_{11} + \dot{p}_{22})$$

denominator in eq. 2-6 is therefore always positive. However, it is very well be that  $\dot{p}_{12} > \dot{p}_{22}$ ; but then because of eq. 2-1  $\dot{p}_{11} > \dot{p}_{12}$ ; this case  $I_2 > I$ ,  $I_1 < 0$ . The current in the first branch flows opposite the input current, an impossible occurrence in normal conduction,<sup>1</sup> or they were derived theoretically by the author,<sup>2</sup> eq. 2-6 including last inference, was confirmed quantitatively by Justi and Zickner.<sup>3</sup> If a current  $I^0$  was already flowing at time  $t = 0$ , with branch currents  $I_1^0$  and  $I_2^0$ , then these currents are superimposed on the system under consideration: in the first branch the current  $I_1 + I_1^0$  will now flow, in second  $I_2 + I_2^0$ . If in particular  $I^0 = -I$ , then, as can easily be puted,  $I_1 + I_1^0 = -(I_2 + I_2^0)$ , and the leads carry no current. erefore if we have introduced a current before cooling down to the rconducting state, and after the cooling we cut off the supply leads, a persistent current remains in the ring consisting of the two branches. recognize here a second method of producing persistent currents. This

Under certain circumstances it may happen that the absolute value of  $I_1$  can be greater than  $I$ .

See Chap. 1, footnote 23.

E. Justi and G. Zickner, *Phys. Z.*, **42**, 258 (1941).

has also been proved experimentally by Justi and Zickner. If we now feed in still another current  $I'$ , then this is independent of the persistent current, and its branch currents  $I'_1$  and  $I'_2$  calculated from eq. 2-6 are superimposed on the persistent current.

(b) Equation 2-4 allows yet another interpretation. If we ask which distribution of the current  $I$  minimizes the magnetic energy  $1/2 \sum_k \dot{p}_{kk} I_k$ , using the Lagrange undetermined multiplier  $\alpha$  we find the conditions

$$\left( \frac{\partial}{\partial I_i} \right) \left( \frac{1}{2} \sum_k \dot{p}_{kk} I_k - \alpha \sum_k I_k \right) = 0$$

$$\sum_k \dot{p}_{ik} I_k = \alpha \quad (i = 1, 2, \dots, n)$$

However, from this and from

$$\sum_k I_k = I$$

we get the same relations between the  $I_k$  and  $I$  as from eq. 2-4. The current distribution in the branched superconducting circuit adjusts itself so as to minimize the magnetic energy. This minimum is, according to eq. 2-6,

$$\frac{1}{2} \frac{\dot{p}_{11} \dot{p}_{22} - \dot{p}_{12}^2}{\dot{p}_{11} + \dot{p}_{22} - 2\dot{p}_{12}} I^2$$

This is important for the understanding of Sizoo's experiments.<sup>4</sup> In fact, in his experiment,  $\dot{p}_{11} \dot{p}_{22} - \dot{p}_{12}^2$  is very nearly zero. On supplying a current, no magnetic field at all is produced — to this approximation; the field strength remains zero at every point in space. If before feeding in  $I$  there are already two currents  $I_1^0$  and  $I_2^0$  flowing in the branches which produce a magnetic field because they are not in the ratio  $I_1 : I_2$ , then this addition of  $I$  does not change anything in the magnetic field; a new field is merely superimposed on the old one, which in our case is zero. This conclusion also remains valid if we choose  $I = -(I_1^0 + I_2^0)$ , i. e., if we simply cut off the leads. All this had been found experimentally by Sizoo in 1926 and it was his work that instigated the discussion presented here.

According to eq. 2-5

$$(\dot{p}_{11} - \dot{p}_{21}) I_1 - (\dot{p}_{22} - \dot{p}_{12}) I_2 = 0$$

In the approximation used here, which allows us to ascribe its own induction coefficient to each of the two unclosed branches (strictly speaking only for closed circuits), the left-hand side of this equation is the flux of induction through the superconducting ring formed by the two branches. The fact that the flux of induction retains its initial value, i. e., zero, even if currents are switched on, corresponds to a theorem which will be discussed in general in Chap. 12.

<sup>4</sup>G. J. Sizoo, Thesis, Leiden, 1926.



(c) The experiments under discussion not only confirm the complete disappearance of the resistances  $r_k$  but also show that there is no noticeable amount of any other energy depending on the current to be added to the magnetic energy. Such an energy would have to be added to the magnetic energy in the principle of least action, equation 2-2, and would disturb the linearity of the relations between the  $I_k$  and  $I$ , if it were a quadratic function of the  $I_k$ . Otherwise it would at least cause the induction coefficients applicable to these experiments to deviate from the  $\rho_k$  values as measured with ohmic currents. Neither possibility occurs in practice. We shall find in Chaps. 5 and 12 that a specific superconduction energy actually does appear, but that in the experiments under discussion and in many other similar experiments, it is far too small an amount to show up against the magnetic energy.

As we indicated in Chap. 1 (c), superconductors have an ohmic resistance or varying currents, in spite of the fact that their d. c. resistance is zero. In the measurements mentioned in this paragraph however the variations are much too slow for this effect to be appreciable.

### CHAPTER 3

#### Fundamental Equations of the Maxwell-London Theory:<sup>2</sup>

(a) In most experimental work we observe effects on the field surrounding the superconductor caused by the phenomena occurring inside the superconductor. To be of any value, therefore, the theory must retain Maxwell's equations for empty space. We shall simplify the Maxwell equations by limiting the discussion to isotropic substances or cubic crystals. This restriction can easily be lifted if necessary, but so far no such necessity has arisen. We therefore introduce the three vectors  $\mathbf{E}$ ,  $\mathbf{D}$ , and  $\mathbf{i}$ , the first of which is the field intensity, the second the displacement, and the third the current density. There exist between them the relations

$$\mathbf{D} = \epsilon \mathbf{E} \quad \mathbf{i} = \sigma \mathbf{E} \quad (3-1)$$

$\epsilon$  dielectric constant  $\epsilon$  and the conductivity  $\sigma$  are positive constants of the material depending only on temperature. For the magnetic field we add three more vectors  $\mathbf{H}$ ,  $\mathbf{B}$ , and  $\mathbf{M}$ , i. e., the field intensity, the magnetic induction, and the induction due to permanent magnetization present in permanent magnets that may be in the field. For these we have the relation

<sup>2</sup>F. London, Une conception nouvelle de la supraconductivité, Paris, 1937.

<sup>3</sup>M. v. Laue, (a) *Ann. Physik*, **42**, 65 (1942); (b) **48**, 223 (1943); (c) **2**, 183 (1948); (d) **31** (1948); (e) **8**, 40 (1948); (f) *Z. Physik*, **125**, 517 (1949).

$$\mathbf{B} = \mu \mathbf{H} + \mathbf{M} \quad (3-2)$$

Here  $\mu$  is a constant depending only on temperature, taken to be unity for ferromagnetics where  $\mathbf{M}$  is not zero. Hysteresis effects are not included in eq. 3-2, it is true, except implicitly in the behavior of  $\mathbf{M}$ . In Lorentz units, which we shall use throughout unless specifically stated otherwise, the Maxwell equations themselves now have the form

$$\begin{aligned} \text{I} \quad \text{curl } \mathbf{E} &= -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} & \text{II} \quad \text{curl } \mathbf{H} &= \frac{1}{c} \left( \frac{\partial \mathbf{D}}{\partial t} + \mathbf{i} \right) \\ \text{III} \quad \text{div } \mathbf{B} &= 0 & \text{IV} \quad \text{div } \mathbf{D} &= \rho \end{aligned}$$

$\rho$  is the space charge density.

(b) For the superconductor we put  $\epsilon = 1$  from the outset, as Maxwell's theory does for all metallic conductors. An important feature of London's generalization is that the permeability  $\mu = 1$ . Moreover,  $\mathbf{M} = 0$ , because no ferromagnetic material shows superconductivity. So  $\mathbf{D}$  coincides with  $\mathbf{E}$  and  $\mathbf{B}$  with  $\mathbf{H}$ . Equations I—IV are simplified to

$$\begin{aligned} \text{I}_s \quad \text{curl } \mathbf{E} &= -\frac{1}{c} \frac{\partial \mathbf{H}}{\partial t} & \text{II}_s \quad \text{curl } \mathbf{H} &= \frac{1}{c} \left( \frac{\partial \mathbf{E}}{\partial t} + \mathbf{i} \right) \\ \text{III}_s \quad \text{div } \mathbf{H} &= 0 & \text{IV}_s \quad \text{div } \mathbf{E} &= \rho \end{aligned}$$

Now — and this introduces something essentially new — the current  $\mathbf{i}$  and the density  $\rho$  are each split into two parts by this theory, namely the ohmic current  $\mathbf{i}^0$  together with the appropriate density  $\rho^0$ , and the supercurrent  $\mathbf{i}^s$  with the corresponding density  $\rho^s$ .

$$\text{V} \quad \mathbf{i} = \mathbf{i}^0 + \mathbf{i}^s \quad \rho = \rho^0 + \rho^s$$

Between each sort of current and the corresponding density we assume a continuity equation:

$$\text{VI} \quad \text{div } \mathbf{i}^0 + \frac{\partial \rho^0}{\partial t} = 0, \quad \text{div } \mathbf{i}^s + \frac{\partial \rho^s}{\partial t} = 0$$

Equation VI gives a definite meaning to the coupling of  $\rho^0$  with  $\mathbf{i}^0$  and of  $\rho^s$  with  $\mathbf{i}^s$ . Only the continuity equation for the total current  $\mathbf{i}$  and the total density  $\rho$  follows in the known way from II<sub>s</sub> and IV<sub>s</sub>. The subdivision carried out here therefore represents an essentially new assumption. Incidentally,  $\rho^0$  shall include not only the contribution from the mobile carriers of the ohmic current  $\mathbf{i}^0$ , but also that from the fixed atoms which is constant in time, and for a homogeneous superconductor uniform in space. This is completely consistent with eq. VI.  $\rho^s$  shall be due only to the carriers of the supercurrent. We are forced to this assertion because in eq. 13-10  $\rho^s$  appears as a factor in a product which can be related only to the supercurrent.

For the ohmic current, Ohm's law, i. e., a linear relationship between  $\mathbf{J}$  and  $\mathbf{E}$ , shall still be valid in superconductors. For a crystal it always is the form

$$\mathbf{J} = \sum_{\beta} \sigma_{\alpha\beta} \mathbf{E}_{\beta} \quad (I)$$

and for mathematical reasons  $\sigma_{\alpha\beta}$  is a tensor of the second rank which we call the conductivity tensor. For cubic crystals it simplifies to a scalar conductivity  $\sigma$ , and eq. VII is replaced by the equation

$$\mathbf{J} = \sigma \mathbf{E} \quad (Ia)$$

The  $\sigma_{\alpha\beta}$  are of the dimensions  $t^{-1}$ . The order of magnitude of  $\sigma$  and likewise principal values  $\sigma_{\alpha\alpha}$  of the tensor for normally conducting pure metals at the low temperatures under discussion is of the order  $10^{19} \text{ sec}^{-1}$ , according to experiments to be described in Chap. 16, we may also ascribe the same order of magnitude to the superconductor in spite of the fact that actual measurements are not available.

Finally, London's fundamental equations for the supercurrent appear essentially new equations in the theory. We formulate them for an arbitrary crystal by associating with the vector  $\mathbf{i}$  a vector  $\mathbf{G}$  for the supermomentum per unit charge and by postulating a linear relation between  $\mathbf{G}$  in terms of the tensors  $\lambda_{\alpha\beta}$  the sums being over  $\alpha, \beta = 1, 2, 3$ :

$$\mathbf{G} = \sum_{\beta} \lambda_{\alpha\beta} \mathbf{i}_{\beta} \quad (II)$$

which simplifies for cubic crystals to read

$$\mathbf{G} = \lambda \mathbf{i} \quad (IIa)$$

And for  $\mathbf{G}$  we introduce the following two differential equations due to London<sup>4</sup>

$$\frac{\partial \mathbf{G}}{\partial t} = \mathbf{E} \quad \text{X} \quad c \text{ curl } \mathbf{G} = -\mathbf{H}$$

According to Chap. 1 (c), London's constant  $\lambda$  is a function of temperature and increases beyond all limit as we approach the transition temperature

<sup>4</sup>This tensor was introduced by M. von Laue (see footnote 2d).

These equations can be combined relativistically in the form

$$c \left( \frac{\partial P_m}{\partial x_n} - \frac{\partial P_n}{\partial x_m} \right) = M_{nm} \quad m, n = 1, 2, 3, 4$$

where  $M_{14} = -iE_1$ , etc.,  $M_{23} = H_1$ , etc., and  $x_4 = ict$ ; the four vector  $\mathbf{P}$  is related to the supermomentum by identifying  $P_{\alpha} = G_{\alpha}$ ,  $\alpha = 1, 2, 3$ , and  $P_4 = 0$  be system at rest.

Here we have written  $x_1, x_2$ , and  $x_3$  for  $x, y, z$ , but this can scarcely lead to any misunderstanding.

from below. The tensor  $\lambda_{\alpha\beta}$  must have the same property. The dimensions of its components are  $[\text{time}]^2$ .

The most general tensor of second rank is asymmetrical, but from Table 1-1 all the crystal classes in which superconductivity has been observed have such high crystallographic symmetry that all tensor constants must be symmetrical, i. e., interchanging their suffixes does not change their value.<sup>5</sup> We therefore put

$$\begin{aligned} \sigma_{\alpha\beta} &= \sigma_{\beta\alpha} \\ \lambda_{\alpha\beta} &= \lambda_{\beta\alpha} \end{aligned} \quad (3-3)$$

In Chap. 13 (b) this will turn out to be a necessary condition for the possibility of superconductivity. It can also be understood in this way why deformations which distort the natural symmetry of the crystals easily destroy the superconductivity — as has often been observed.

We shall find in Chap. 5 that

$$\frac{1}{2} (\mathbf{i} \cdot \mathbf{G}) = \frac{1}{2} \sum_{\alpha\beta} \lambda_{\alpha\beta} \mathbf{i}_{\alpha} \mathbf{i}_{\beta} \quad (3-4)$$

is the density of the free energy that is connected with the supercurrent. By requiring that it be positive, not only in the cubic system where it equals  $\frac{1}{2} \lambda (\mathbf{i})^2$ , but also under all circumstances, we conclude that the components  $\lambda_{\alpha\alpha}$  with two identical suffixes, the determinant of all the  $\lambda_{\alpha\beta}$ , and the three symmetrical subdeterminants

$$\begin{vmatrix} \lambda_{\alpha\alpha} & \lambda_{\alpha\beta} \\ \lambda_{\beta\alpha} & \lambda_{\beta\beta} \end{vmatrix}$$

are all positive. These are the necessary and sufficient conditions that the quadratic form  $\sum_{\alpha\beta} \lambda_{\alpha\beta} \mathbf{i}_{\alpha} \mathbf{i}_{\beta}$  shall be positive and definite. But as  $\sum_{\alpha\beta} \sigma_{\alpha\beta} \mathbf{E}_{\alpha} \mathbf{E}_{\beta}$  is also positive and definite (it is the expression for the Joule heat, see Chap. 5), the conductivity tensor obeys the same conditions. The quadratic surfaces corresponding to these tensors:

$$\sum_{\alpha\beta} \lambda_{\alpha\beta} x_{\alpha} x_{\beta} = \text{constant} \quad \text{and} \quad \sum_{\alpha\beta} \sigma_{\alpha\beta} x_{\alpha} x_{\beta} = \text{constant}$$

are therefore ellipsoids. If their axes are chosen as coordinates, then all the tensor components with unlike suffixes vanish, and those with two like suffixes give the principal values  $\lambda_1, \lambda_2, \lambda_3$  of the tensor.

In the crystal classes in which superconductivity has been detected to date (Table 1-1) the axes of these ellipsoids are completely fixed and

<sup>5</sup>This is also true for all superconducting compounds and alloys. Compare Max von Laue, footnote 2c; in this reference, a table appears giving all crystal classes together with the properties of all second-rank tensors that can belong to them, like the tensors  $\lambda_{\alpha\beta}$  and  $\sigma_{\alpha\beta}$ , that can form a linear relation between two polar vectors. In these particular cases the polar vectors are  $\mathbf{i}$  and  $\mathbf{G}$ ,  $\mathbf{P}$ , and  $\mathbf{E}$ .

incide with the principal crystallographic axes. In the rhombic system, e., for gallium and uranium, they are mutually perpendicular but not equal length. In the tetragonal and hexagonal systems the surfaces are ipsoids of revolution whose unequal axes coincide with the principal crystallographic axes. Therefore two of the principal values of the tensor are equal. We need scarcely mention the cubic system for which the ipsoid degenerates into a sphere.

As the determinant of  $\lambda_{\alpha\beta}$  differs from zero the three equations VIII can be solved for the components  $\dot{\mathbf{r}}_{\alpha}$ . Thus not only does it follow from  $\dot{\mathbf{r}} = 0$  that  $\mathbf{G} = 0$ , but also conversely from  $\mathbf{G} = 0$  that  $\dot{\mathbf{r}} = 0$ .

It is a significant feature of this theory that the ohmic current and supercurrent are essentially independent of each other and are only coupled in a secondary way through the magnetic field with which they both related.

The fundamental equations of this chapter are not all independent. Equation III<sub>1</sub> is given by forming the divergence of X; eq. I, by forming curl of eq. IX and using eq. X. Nevertheless by retaining eqs. I, and III<sub>1</sub> show more clearly that the London theory does not do away with the Maxwell theory, but only supplements it. There is no contradiction in the set of equations.

(c) In addition to the differential equations, the theory still needs to be completed by boundary conditions at all surfaces where the constants of the theory undergo sudden changes, as at the surface of the specimen. The boundary conditions do not represent new additions; they are limiting cases of the differential equations themselves. For instance  $\mathbf{B}$ ,  $\mathbf{D}$ , and  $\mathbf{i}$  are finite time derivatives everywhere, and hence eqs. I and II lead to the Stokes' theorem regarded as applying to a "surface curl" to the surface. Also, according to eq. III we may say that the "surface divergence" of  $\mathbf{B}$  is zero; therefore if we indicate two opposite normals to the surface of discontinuity by  $\mathbf{n}_1$  and  $\mathbf{n}_2$  we obtain

$$\mathbf{B}_{n_1} + \mathbf{B}_{n_2} = 0 \quad (3-5)$$

Similarly, according to eq. IV, when a surface charge density exists we have

$$\mathbf{D}_{n_1} + \mathbf{D}_{n_2} = \rho \quad (3-6)$$

These two equations hold for the superconductor if we replace  $\mathbf{B}$  by  $\mathbf{H}$  and  $\mathbf{D}$  by  $\mathbf{E}$ . The following new boundary conditions then have to be added: regarding to the continuity equations in eq. VI the surface divergences of the current densities  $\dot{\mathbf{r}}^0$  and  $\dot{\mathbf{r}}^s$  are related to the surface charge densities and  $\rho^s$  by the equations:

$$\dot{\mathbf{r}}_{n_1}^0 + \dot{\mathbf{r}}_{n_2}^0 = \frac{\partial \rho^0}{\partial t} \quad \dot{\mathbf{r}}_{n_1}^s + \dot{\mathbf{r}}_{n_2}^s = \frac{\partial \rho^s}{\partial t} \quad (3-7)$$

Since  $\mathbf{H}$  is finite everywhere, eq. X requires that the tangential components of  $\mathbf{G}$  be everywhere continuous across every surface:

$$\mathbf{G}_n = \mathbf{G}_t \quad (3-8)$$

This means that at the boundary between two cubic crystal superconductors

$$\lambda_1 \dot{\mathbf{r}}_1 = \lambda_2 \dot{\mathbf{r}}_2 \quad (3-9)$$

The superconductor with the smaller  $\lambda$  carries the higher tangential current; it behaves as if it were the better superconductor. Increasing temperature increases the constant, as already stated, thus impairing the superconductor.

(d) Although, as already mentioned, we shall generally use Lorentz units, we have also enumerated the changes involved in the transition to electrostatic units. In these units the fundamental eqs. II and IV become

$$\text{curl } \mathbf{H} = \frac{1}{c} \left( \frac{\partial \mathbf{D}}{\partial t} + 4\pi \mathbf{i} \right) \quad \text{and} \quad \text{div } \mathbf{D} = 4\pi \rho$$

Equations I, III, and VII remain unchanged. In general, the transformation is effected by the equations:

$$\begin{aligned} \rho_{L_s} &= \sqrt{4\pi} \rho_{E_s}, & \mathbf{i}_{L_s} &= \sqrt{4\pi} \mathbf{i}_{E_s}, & \mathbf{E}_{L_s} &= \frac{\mathbf{E}_{E_s}}{\sqrt{4\pi}}, \\ \mathbf{H}_{L_s} &= \frac{\mathbf{H}_{E_s}}{\sqrt{4\pi}}, & \mathbf{B}_{L_s} &= \frac{\mathbf{B}_{E_s}}{\sqrt{4\pi}}, & (\sigma_{\alpha\beta})_{L_s} &= 4\pi (\sigma_{\alpha\beta})_{E_s} \end{aligned} \quad (3-10)$$

The question arises: shall the tensor components  $\lambda_{\alpha\beta}$  have the same values in both systems so that  $\mathbf{G}_{L_s} = \sqrt{4\pi} \mathbf{G}_{E_s}$  and the eqs. IX and X have to be replaced by

$$4\pi \frac{\partial \mathbf{G}_{E_s}}{\partial t} = \mathbf{E} \quad \text{and} \quad 4\pi c \text{curl } \mathbf{G}_{E_s} = -\mathbf{H}?$$

We decide instead in favor of taking over eqs. IX and X unchanged in the electrostatic system and derive the transformations:

$$\mathbf{G}_{L_s} = \frac{\mathbf{G}_{E_s}}{\sqrt{4\pi}}, \quad (\lambda_{\alpha\beta})_{L_s} = \frac{(\lambda_{\alpha\beta})_{E_s}}{4\pi} \quad (3-11)$$

We shall find out the advantages of this convention in Chaps. 15 and 16. There the pure number  $\nu \sigma \lambda$ , where  $\nu$  is a frequency, has the same value in both systems of units, and plays an important part in the theory of oscillations similar to the part played by the scalar product  $(\dot{\mathbf{r}} \cdot \mathbf{G})$  in what follows.

(e) Even though we intend to present London's theory in a phenomenological manner, we wish nevertheless to point out the atomic theory basis from which it developed historically. Fritz and Heinz London<sup>6</sup> attempted in 1935 to make the fundamental eqs. IX and X, which they wrote in the form

$$\text{IX}_a \quad \frac{\partial \dot{\mathbf{r}}}{\partial t} = \mathbf{E} \quad \text{IX}_b \quad c \text{curl } (\dot{\mathbf{r}} \cdot \mathbf{r}) = -\mathbf{H}$$

<sup>6</sup>F. and H. London, *Physica*, 2, 241 (1935).

is plausible from quantum theoretical considerations. In this way they find a relation between the constant  $\lambda$  and the charge  $e$ , the mass  $m$  of the electron, and the number  $N$  of the superconducting electrons per unit volume, namely,

$$\lambda = \frac{m}{e^2 N} \quad (3-12)$$

However, eq. IXa had already been derived in 1933 by Becker, Heller, Sauter<sup>7</sup> on a purely mechanical basis. They took the electric field as the only force acting on the electron, so that

$$m \frac{dv}{dt} = eE$$

where  $v$  is the velocity of the electron. Furthermore, as the current density is  $eNv$  one arrives at eqs. IXa and 3-12 if one neglects the difference between the partial time derivative  $\partial/\partial t$  (at constant coordinates) and  $d/dt$  (referring to a moving particle); this is permissible for sufficiently small velocities. Equation IXa can be derived from eq. IXa by means of Maxwell's equation 1 under the physically self-evident assumption that no field existed prior to a certain time 0. Thus if one takes the curl of eq. IXa and integrates from  $t = 0$  to  $t$ , one gets:

$$\text{curl}(\lambda v) = \int_0^t \text{curl} E dt = -\frac{1}{c} \mathbf{H}$$

to the extent this entire theory was contained in the "acceleration theory" of Becker and co-workers.

One shall not go further into this atomic picture here although in Chap. 13 we shall make use of the picture to explain the Maxwell-London stresses, pointing out that neither the lattice formed by the ions nor the ohmic conduction electrons exert any force on the mechanism of the supercurrent.

One makes a rough estimate of  $\lambda$  from 3-12 if we take aluminum as an example. The lattice cell contains four atoms and has an edge of  $4 \times 10^{-8}$  cm. The cubic centimeter therefore contains  $1.6 \times 10^{22}$  cells and  $6.4 \times 10^{22}$  atoms. If we assume the number  $N$  of superconducting electrons to be the same as the number of atoms,  $N = 6.4 \times 10^{22}$  cm<sup>-3</sup>, and  $e = 4.8 \times 10^{-10}$  esu, with  $m = 9 \times 10^{-28}$  gm, and  $e\lambda = \sqrt{4\pi eE} = \sqrt{4\pi \times 4.8 \times 10^{-10} \times 10^{-10}}$  Lorentz unit, it follows that

$$\lambda_L = 2 \times 10^{-32} \text{ sec}^2 \quad (3-13)$$

according to 3-11.

$$\lambda_{EL} = 2.5 \times 10^{-31} \text{ sec}^2$$

Probably the number  $N$  is much smaller, and  $\lambda$  accordingly greater.

<sup>7</sup> Becker, G. Heller, and F. Sauter, *Z. Physik*, **85**, 772 (1933).

## CHAPTER 4

## Space Charges in Superconductors

Space charges may be formed in a superconductor by irradiating it with fast cathode rays which are sooner or later trapped inside the superconductor. The theory must lead to plausible conclusions about the future of such charges, and this requirement has played a role in its development. We assume the crystal to be cubic,  $\lambda$  and  $\sigma$  constants in space and time. From eqs. VI, IXa, and IVa respectively there follow the equations

$$\frac{\partial^2 \rho^0}{\partial t^2} = -\text{div} \frac{\partial v}{\partial t} = -\frac{1}{\lambda} \text{div} E = -\frac{\rho}{\lambda} = -\frac{(\rho^0 + \rho^s)}{\lambda}$$

while from eqs. IV, VIIa, and VI correspondingly

$$\rho = \text{div} E = \frac{1}{\sigma} \text{div} i^0 = -\frac{1}{\sigma} \frac{\partial \rho^0}{\partial t}$$

Therefore the differential equations

$$\frac{\partial^2 \rho^0}{\partial t^2} + \frac{(\rho^0 + \rho^s)}{\lambda} = 0 \quad \frac{\partial \rho^0}{\partial t} + \sigma(\rho^0 + \rho^s) = 0 \quad (4-1)$$

hold for the two unknowns  $\rho^s$  and  $\rho^0$ . They are solved under the assumption that

$$\rho^0 = \rho^0 e^{-\alpha t} \quad \rho^s = \rho^s e^{-\alpha t} \quad (4-2)$$

which transform the differential equations into the algebraic relations

$$(\alpha^2 + \lambda^{-1}) \rho^s + \lambda^{-1} \rho^0 = 0 \quad (4-3)$$

$$\sigma \rho^s + (\sigma - \alpha) \rho^0 = 0$$

Putting the determinant of the coefficients equal to zero yields for  $\alpha$  the equation

$$\alpha^3 - \sigma \alpha^2 + \lambda^{-1} \alpha = 0 \quad (4-4)$$

To each root of this equation there corresponds a certain ratio  $\rho^s/\rho^0$ . Carrying through the calculation gives

$$\alpha_1 = \frac{1}{2} (\sigma + \sqrt{\sigma^2 - 4\lambda^{-1}}), \quad \left( \frac{\rho^s}{\rho^0} \right)_1 = -\frac{1}{2} \left( 1 - \sqrt{1 - \frac{4}{\sigma^2 \lambda}} \right)$$

$$\alpha_2 = \frac{1}{2} (\sigma - \sqrt{\sigma^2 - 4\lambda^{-1}}), \quad \left( \frac{\rho^s}{\rho^0} \right)_2 = -\frac{1}{2} \left( 1 + \sqrt{1 - \frac{4}{\sigma^2 \lambda}} \right) \quad (4-5)$$

$$\alpha_3 = 0, \quad \left( \frac{\rho^s}{\rho^0} \right)_3 = -1$$

$$\alpha_3 = 0, \quad \left( \frac{\rho^s}{\rho^0} \right)_3 = -1$$

The general solution of eq. 4-1 therefore reads

$$\rho^0 = A_1 e^{-\alpha_1 t} + A_2 e^{-\alpha_2 t} + A_3$$

$$\rho^s = -\frac{1}{2} \left( 1 - \sqrt{1 - \frac{4}{\sigma^2 \lambda}} \right) A_1 e^{-\alpha_1 t} - \frac{1}{2} \left( 1 + \sqrt{1 - \frac{4}{\sigma^2 \lambda}} \right) A_2 e^{-\alpha_2 t} - A_3$$

$A_1, A_2, A_3$  are constants of integration, i. e., invariable with time, but otherwise arbitrary functions of position.  $\alpha_1$  and  $\alpha_2$  can be complex, but other roots always have real parts. When  $\alpha_1$  and  $\alpha_2$  are complex, there are superposed vibrations of  $\rho^0$  and  $\rho^s$  which decay with time until  $\rho = \rho^0 + \rho^s$  becomes zero. The equations do not require that the individual densities  $\rho^0$  and  $\rho^s$  each vanish. This is related to the fact that the two mechanisms of conduction are independent, being coupled only by the field which has already disappeared in the final state when the total density  $\rho = 0$ .

On the whole the phenomenological theory does not say anything about individual densities in the final state, except that where a current  $\mathbf{j}$  is flowing,  $\rho^s$  cannot be zero. Otherwise the momentum  $\rho^s \lambda \mathbf{j}$  of the supercurrent, which we shall meet with in eq. 13-10, should equally well be zero. Because the field equations are linear, the decay of  $\rho$  takes place independently of, and is superimposed upon, all other processes that occur in the superconductor. When we investigate these other processes, therefore, we neglect the space charge completely and always put  $\text{div } \mathbf{E} = 0$  place of IV.

In order to do this it is necessary that  $\sigma$  and  $\lambda$  do not change in time or place. If these constants were to vary because of temperature inequalities for example, or varying composition of an alloy, then the space charges would change according to other laws. Nevertheless in a stationary state the superconductor is charge free under all circumstances. From eq. VIII it follows, namely, that if  $\partial/\partial t = 0$ , then  $\mathbf{E} = 0$ , and therefore according to eq. IV,  $\sigma = 0$ . The above calculation cannot be applied to a noncubic crystal where  $\sigma$  is a symmetrical tensor. However, in the next chapter we will see how we can also draw conclusions about the decay in this case. In a normal conductor with a cubic lattice the charge decays according to eq. III. This can be seen by forming the divergence of eq. III. This result is well known, but having regard to the magnitude of  $\sigma$  it is doubtful whether Maxwell theory will still be valid for such a rapid decay. It is also doubtful in our theory of superconductivity. However, it is significant that the theory does lead to plausible results, and its conclusions about decay should be at least qualitatively correct.

## CHAPTER 5

### The Conservation of Energy

a) We obtain the energy principle for the space outside the superconductor in the known manner by forming the scalar product of eq. I  $(-\mathbf{H})$  and of II with  $\mathbf{E}$ , adding the results and applying the rule

$$(\mathbf{P} \cdot \text{curl } \mathbf{Q}) - (\mathbf{Q} \cdot \text{curl } \mathbf{P}) = \text{div } [\mathbf{Q} \times \mathbf{P}] \quad (5-1)$$

The result is immediately

$$-c \text{div } [\mathbf{E} \times \mathbf{H}] = \left( \mathbf{E} \cdot \frac{\partial \mathbf{D}}{\partial t} \right) + \left( \mathbf{H} \cdot \frac{\partial \mathbf{B}}{\partial t} \right) + (\mathbf{E} \cdot \mathbf{j}) \quad (5-2)$$

According to eqs. 3-1 and 3-2 and because  $\partial \mathbf{M} / \partial t = 0$ , this takes the form

$$\frac{\partial}{\partial t} \left( \frac{1}{2} \epsilon \mathbf{E}^2 + \frac{1}{2} \mu \mathbf{H}^2 \right) + \sigma \mathbf{E}^2 + c \text{div } [\mathbf{E} \times \mathbf{H}] = 0 \quad (5-3)$$

Within the differential sign are the density of electrical energy  $\frac{1}{2} \epsilon \mathbf{E}^2$  and of magnetic energy  $\frac{1}{2} \mu \mathbf{H}^2$ ;  $\sigma \mathbf{E}^2$  gives the Joule heat per unit time, and  $c [\mathbf{E} \times \mathbf{H}]$  is the flux density of electromagnetic energy, the so-called Poynting vector.

Proceeding in the same manner with eqs. I, and II, we find for the interior of the superconductor, instead of eq. 5-2

$$-c \text{div } [\mathbf{E} \times \mathbf{H}] = \left( \mathbf{E} \cdot \frac{\partial \mathbf{E}}{\partial t} \right) + \left( \mathbf{H} \cdot \frac{\partial \mathbf{H}}{\partial t} \right) + (\mathbf{E} \cdot \mathbf{j}^0) + (\mathbf{E} \cdot \mathbf{j}^s) \quad (5-4)$$

or, also according to eqs. VII, VIII, and IX

$$\frac{\partial}{\partial t} \left( \frac{1}{2} \mathbf{E}^2 + \frac{1}{2} \mathbf{H}^2 + \frac{1}{2} \sum_{\alpha\beta} \lambda_{\alpha\beta} \mathbf{i}_\alpha \cdot \mathbf{i}_\beta \right) + \sum_{\alpha\beta} \sigma_{\alpha\beta} \mathbf{E}_\alpha \mathbf{E}_\beta + c \text{div } [\mathbf{E} \times \mathbf{H}] = 0 \quad (5-5)$$

In a superconductor there is, in addition to the electric and magnetic energy, a specific energy of the supercurrent having a density

$$\frac{1}{2} \sum_{\alpha\beta} \lambda_{\alpha\beta} \mathbf{i}_\alpha \cdot \mathbf{i}_\beta = \frac{1}{2} (\mathbf{j}^0 \cdot \mathbf{G}) \quad (5-6)$$

or, for the cubic case

$$\frac{1}{2} \lambda \mathbf{j}^2 \quad (5-7)$$

This is the only difference from the older theory. If we wish to combine the laws of conservation, eqs. 5-3 and 5-5, which will be useful later, we put

$$\frac{1}{2} \epsilon \mathbf{E}^2 + \frac{1}{2} \mu \mathbf{H}^2 + \frac{1}{2} (\mathbf{j}^0 \cdot \mathbf{G}) \quad (5-8)$$

for the total energy density. Our assumptions in Chap. 3 (b) about the tensors  $\lambda$  and  $\sigma$  ensure that the two sums in eq. 5-5 are always positive. Therefore it follows from eq. 5-5 that the energy of any electric field will be entirely dissipated by Joule heat if energy is not supplied from outside. Therefore if the superconductor does contain space charges, they must vanish. For if they were assumed to remain, there would exist an electric field without a magnetic field strength: the Poynting vector would be zero, and according to eq. 5-5 the field energy would decrease until the field and therefore also its charges become zero, contradicting the hypothesis. The conclusion drawn in Chap. 4 about the decay of the total space charge density  $\rho$  in superconductors with a cubic lattice structure is in this way applicable to all superconductors.

Stationary magnetic fields are, however, possible in which a supercurrent appears but no electric field strength. In deriving the energy law,

1. 5-5, it is assumed that the  $\lambda_{\alpha\beta}$  do not change with time, just as in 1. 5-2  $\epsilon$  and  $\mu$  have to be constant. All these constants of the material depend on temperature. Therefore eqs. 5-2 and 5-5 can be used for other thermal processes only. The kinds of energy appearing here are therefore free energies in the sense of thermodynamics. The actual energy  $E$  connected with the free energy  $F$  by the relation  $E = F - T \partial F / \partial T$ . Consequently the energy of the supercurrent per unit volume is

$$\frac{1}{2} \sum_{\alpha\beta} \left( \lambda_{\alpha\beta} - T \frac{\partial \lambda_{\alpha\beta}}{\partial T} \right) \mathbf{i}_{\alpha} \cdot \mathbf{i}_{\beta}$$

for the cubic case

$$\frac{1}{2} \left( \lambda - T \frac{\partial \lambda}{\partial T} \right) \mathbf{i}^2$$

versing signs, the second terms, i. e., the expressions

$$\frac{1}{2} T \sum_{\alpha\beta} \frac{\partial \lambda_{\alpha\beta}}{\partial T} \mathbf{i}_{\alpha} \cdot \mathbf{i}_{\beta} \quad \text{or} \quad \frac{1}{2} T \frac{\partial \lambda}{\partial T} \mathbf{i}^2$$

represent the heat which has to be removed from the superconductor during thermal production of the supercurrent  $\mathbf{i}$ . As  $\lambda$  increases with  $T$  they are positive, and immediately below the transition temperature they are to be considerable.

## CHAPTER 6

### The Telegrapher's Equation for Superconductors with Cubic Crystal Structure

It is known that by eliminating all field vectors but one from among Maxwell's field equations one obtains a partial differential equation for the remaining vector, the so-called telegrapher's equation which occupies a position intermediate between the wave equation  $\Delta u - (1/c^2) \partial^2 u / \partial t^2 = 0$  and the equation for heat conduction  $\Delta u - k^2 \partial u / \partial t = 0$ . We now intend to perform this elimination for the superconductivity theory. We assume all constants of the material to be unvarying in time and space. The lattice shall be cubic. We form the curl of II<sub>1</sub>. Then from the rule

$$\text{curl curl } \mathbf{P} = \text{grad div } \mathbf{P} - \Delta \mathbf{P} \quad (6-1)$$

This is the Helmholtz free energy  $F = E - TS$ , not the Gibbs free energy  $E - TS + PV + HM$ .

## 6. THE TELEGRAPHER'S EQUATION

and according to III<sub>1</sub> we obtain  $-\Delta \mathbf{H}$  on the left-hand side. The result is therefore:

$$-\Delta \mathbf{H} = \frac{1}{c} \left\{ \text{curl} \frac{\partial \mathbf{E}}{\partial t} + \text{curl} \mathbf{i}^0 + \text{curl} \mathbf{i} \right\}$$

We transform the right-hand side of this by means of eqs. I<sub>1</sub>, VII, and IX; the first term yields  $-(1/c^2) \partial^2 \mathbf{H} / \partial t^2$ , the second  $-(\sigma/c^2) \partial \mathbf{H} / \partial t$ , and the third  $-\mathbf{H}/c^2 \lambda$ . Consequently

$$W(\mathbf{H}) \equiv \Delta \mathbf{H} - \frac{1}{c^2} \frac{\partial^2 \mathbf{H}}{\partial t^2} - \frac{\sigma}{c^2} \frac{\partial \mathbf{H}}{\partial t} - \frac{\mathbf{H}}{c^2 \lambda} = 0 \quad (6-2)$$

Now we form the curl of eq. I<sub>1</sub>. Because of IV<sub>1</sub> with  $\rho = 0$  the only term we get on the left-hand side is  $-\Delta \mathbf{E}$ . By using eqs. II<sub>1</sub> and VII<sub>1</sub>, then eqs. VIII and IX we reduce the right-hand side to

$$\begin{aligned} -\frac{1}{c} \text{curl} \frac{\partial \mathbf{H}}{\partial t} &= -\frac{1}{c^2} \left( \frac{\partial^2 \mathbf{E}}{\partial t^2} + \frac{\partial \mathbf{i}^0}{\partial t} + \frac{\partial \mathbf{i}}{\partial t} \right) \\ &= -\frac{1}{c^2} \left( \frac{\partial^2 \mathbf{E}}{\partial t^2} + \sigma \frac{\partial \mathbf{E}}{\partial t} + \frac{\mathbf{E}}{\lambda} \right) \end{aligned}$$

Consequently

$$W(\mathbf{E}) \equiv \Delta \mathbf{E} - \frac{1}{c^2} \left( \frac{\partial^2 \mathbf{E}}{\partial t^2} + \sigma \frac{\partial \mathbf{E}}{\partial t} + \frac{\mathbf{E}}{\lambda} \right) = 0 \quad (6-3)$$

If we again form the curl of eq. 6-2 it follows because of eq. II<sub>1</sub>, and because the operator  $W$  can be interchanged with the operation of forming the curl:

$$W \left( \frac{\partial \mathbf{E}}{\partial t} + \mathbf{i} \right) = 0$$

By combining this with eq. 6-3 differentiated with respect to  $t$ , one gets

$$W(\mathbf{i}) = 0$$

On the other hand, multiplying eq. 6-3 by  $\sigma$  and using eq. VII give

$$W(\mathbf{i}^0) = 0 \quad (6-4)$$

Consequently by subtracting the last two equations, one finds from eq. V

$$W(\mathbf{i}) = 0 \quad (6-5)$$

The generalized telegrapher's equation  $W(u) = 0$  therefore holds for each component of any of the field vectors with respect to cartesian coordinates. If the vectors were resolved in terms of curvilinear coordinates special treatment would be necessary.

Most experiments with superconductivity deal with stationary fields, so that their study constitutes the most important part of the theory. For

case the equation for  $W(u)$  is reduced to its first and its last terms: are left with the differential equation

$$\Delta u - \beta^2 u = 0 \quad (6-6)$$

re  $u$ , as stated, represents a component of any field vector and where

$$\beta^2 = \frac{1}{c^2 \lambda} \quad (6-7)$$

os. 7 and 11 will deal with this differential equation.

All the above is expressed in Lorentz units. In electrostatic units the two terms in eq. 6-1 gain a factor  $4\pi$ . So in place of eq. 6-7

$$\beta^2 = \frac{4\pi}{c^2 \lambda} \quad (\text{in esu}) \quad (6-8)$$

rding to eq. 3-11  $\beta$  has the same value in both systems of units.

## CHAPTER 7

### Stationary Fields

As mentioned in Chap. 4 it follows from eq. IX that  $E = 0$  in the nary case. Furthermore by eq. I<sub>a</sub>,  $E$  is the gradient of a scalar tial and so the superconductor is a region of constant potential even the tensor components  $\lambda_{ab}$  vary with position in space. By eq. VII is no ohmic current; it is deprived of its potential gradient by the ice of the supercurrent, i. e., it is short circuited. Therefore no ment using direct current can enable us to detect the finite con-ity of the superconductor. The only significant field vectors are urrent  $\mathbf{j}$  and the magnetic field  $\mathbf{H}$ . These vectors are more strongly d than in the normal conductor, because there exists between them ly the generally valid relation II, which here simplifies to

$$\text{curl } \mathbf{H} = \frac{\mathbf{j}}{c} \quad (7-1)$$

so eq. IX applying specifically to superconductors:

$$\text{curl } \mathbf{G} = -\frac{\mathbf{H}}{c}, \quad \left( \mathbf{G}_a = \sum_b \lambda_{ab} i_b^0 \right) \quad (7-2)$$

hing we can say about the stationary case is based on the combined tion of these two laws. This excludes the possibility of a current-agnetic-potential field in a normal conductor. From  $\text{curl } \mathbf{H} = 0$  ws that  $\mathbf{j} = 0$ ,  $\mathbf{G} = 0$ , and  $\mathbf{H} = 0$ . Strictly speaking there is no

outside field into which one could place a superconductor carrying a current. The current distribution changes with any attempt to do so in such a way as to annul the outside field. It is possible to keep the current strength constant, and if one considers only the total current strength, one may use the term "external field". In the following sections we shall follow this through for the superconductor with cubic crystal structure.

In many of the examples to be considered the field inside the superconductor is desired when the field in the surrounding space is known. It follows from a general theorem that the solution is unique. In fact, if we form the scalar product of eq. 7-1 with  $\mathbf{G}$  and of eq. 7-2 with  $(-\mathbf{H})$ , add the two, and apply the rule 5-1, we obtain

$$\text{div } [\mathbf{H} \times \mathbf{G}] = \frac{1}{c} \{ (\mathbf{j} \cdot \mathbf{G}) + \mathbf{H}^2 \} \quad (7-3)$$

Integrating eq. 7-3 over the volume of the superconductor and using Gauss' theorem<sup>1</sup>

$$\int_S \text{div } [\mathbf{H} \times \mathbf{G}] d\tau = - \int_S [\mathbf{H} \times \mathbf{G}]_{n_i} d\sigma$$

we get

$$\frac{1}{c} \int_S \{ (\mathbf{j} \cdot \mathbf{G}) + \mathbf{H}^2 \} d\tau = \int_S [\mathbf{G} \times \mathbf{H}]_{n_i} d\sigma \quad (7-4)$$

The suffix  $S$  below the integral signs indicates that the volume integral extends over the volume of the superconductor and the surface integral over its entire surface.<sup>2</sup>

Now the normal component of the vector product  $[\mathbf{G} \times \mathbf{H}]$  contains only the tangential components of  $\mathbf{G}$  and  $\mathbf{H}$ . If either  $\mathbf{G}_t = 0$  or  $\mathbf{H}_t = 0$  over the whole surface, then the right side of eq. 7-4 is zero. The left side, however, vanishes only if  $\mathbf{H} = 0$  and  $\mathbf{G} = 0$  or  $\mathbf{j} = 0$  at every point of the superconductor.

Consider two fields  $\mathbf{H}^{(1)}$ ,  $\mathbf{j}^{(1)}$  and  $\mathbf{H}^{(2)}$ ,  $\mathbf{j}^{(2)}$  which coincide everywhere over the boundary either with respect to  $\mathbf{H}_{\text{tang}}$  or to  $\mathbf{G}_{\text{tang}}$ . Equation 7-4

<sup>1</sup>  $n_i$  indicates the inner normal on the surface  $d\sigma$ .

<sup>2</sup> If one uses the Gauss theorem for multiply connected regions, as we do later in Chap. 12, it is first necessary to produce singly connected regions by making a sufficient number of cuts and adding the new cross sections to the surface. Sometimes the cross sections make appreciable contributions. Here this is not the case because  $\mathbf{G}$  and  $\mathbf{H}$  are singlevalued functions of position, so that the contributions from both sides of any cross section cancel each other. Equation 7-4 therefore holds also for multiply connected superconductors.

<sup>3</sup> According to eq. 3-4,  $(\mathbf{j} \cdot \mathbf{G})$  is necessarily positive with the exception of the case where  $\mathbf{j} = 0$ ,  $\mathbf{G} = 0$ .

is equally well for the difference field  $\mathbf{H}' = \mathbf{H}^{(1)} - \mathbf{H}^{(2)}$ ;  $\mathbf{j}' = \mathbf{j}^{(1)} - \mathbf{j}^{(2)}$  use all our differential equations are linear; it follows then that the reference field vanishes throughout the volume:  $\mathbf{H}' = 0$ ,  $\mathbf{j}' = 0$ . The stationary field in a superconductor is therefore uniquely determined by tangential components at its surface of either the magnetic field or the electromagnetic momentum of the supercurrents. This corresponds to the theorem of potential theory according to which the potential in a region is uniquely fixed by its tangential components over the surface; these fix the surface potential to within an additive constant, this in turn fixes the potential in the interior. The vectors  $\mathbf{G}$  and  $\mathbf{H}$  on the right-hand side of eq. 7-4 here refer to the inner side of the surface. It is also possible here to insert for  $\mathbf{H}$  its value on the outside of the surface because by Chap. 3 (c) the tangential component of  $\mathbf{H}$  is continuous across the surface. In this way the field in the interior is uniquely determined by the external magnetic field.

For the homogeneous superconductor with a cubic lattice, eq. 7-2 can be simplified to read

$$\lambda \operatorname{curl} \mathbf{j} = -\frac{1}{c} \mathbf{H} \quad (7-5)$$

we form the curl of eq. 7-1, then the fundamental eq. III, and -5 together with the theorem 6-1 give us

$$\Delta \mathbf{H} - \beta^2 \mathbf{H} = 0, \quad \beta^2 = \frac{1}{c^2 \lambda} \quad (7-6)$$

inversely, if we form the curl of eq. 7-5, then use eqs. VI and 7-1, we get

$$\Delta \mathbf{j} - \beta^2 \mathbf{j} = 0 \quad (7-7)$$

we come back at once to eqs. 6-6 and 6-7.

The simplest conceivable example is that of a superconductor; one half of space  $z > 0$ , so having the plane  $z = 0$  as its boundary. Outside space  $z < 0$ , there is a homogeneous magnetic field  $\mathbf{H}^0$ , then -6 can be solved by putting

$$\mathbf{H} = \mathbf{H}^0 e^{-\beta z} \quad (7-8)$$

use  $\operatorname{div} \mathbf{H} = 0$ ,  $\mathbf{H}_z^0$  must be zero. We can turn the  $x$  and the (perpendicular)  $y$  directions in such a manner that  $\mathbf{H}_x^0$  also vanishes. Then it is that for the field strength in the superconductor

$$\mathbf{H}_x = \mathbf{H}_z = 0, \quad \mathbf{H}_y = H^0 e^{-\beta z} \quad (7-9)$$

fore according to eq. 7-1 the equations<sup>4</sup>

$$\begin{aligned} i_x &= -c \frac{\partial H_y}{\partial z} = \beta c H^0 e^{-\beta z} = \lambda^{-1/2} H^0 e^{-\beta z} \\ i_y &= i_z = 0 \end{aligned} \quad (7-10)$$

<sup>4</sup> electrostatic units  $i_x = H^0 e^{-\beta z} / \sqrt{4\pi\lambda}$ , compare eqs. 3-10 and 3-12.

represent the supercurrent vector field. We gather from this that the current density at the surface depends only on the field strength  $H^0$  there,  $i_x$ ,  $\mathbf{H}$ , and the inner normal of the superconductor are perpendicular to each other and form a right-handed system like the coordinate system  $x, y, z$  adopted here. The field penetrates the superconductor only to a depth of the order of magnitude  $\beta^{-1}$ . It forms a protecting layer of that thickness under which lies a region protected from the influence of the field. This result is fundamental because it can be taken over for the case of curved surfaces provided only that the superconductor is thick compared with the penetration depth  $\beta^{-1}$ . In this lies the explanation of the Meissner effect.

The surface density of the current is

$$i_s = \int_0^\infty i_x dz = c H^0 \quad (7-11)$$

In electrostatic units eq. 7-11 reads, by eq. 3-10

$$i_s = \frac{c H^0}{4\pi}$$

and if the current is measured in amperes,  $i_s = 10 H^0 / 4\pi$ ; nearly 80 amp are flowing per centimeter across each magnetic line of force at  $H^0 = 100$  oersteds. The penetration depth is

$$\beta^{-1} = c \sqrt{\lambda} \quad (7-12)$$

or  $\beta^{-1} = c \sqrt{\lambda / 4\pi}$  in electrostatic units, by eq. 7-6. It is of the order of magnitude  $10^{-5}$  cm if we assume for  $\lambda$  the order of magnitude  $10^{-31} \text{ sec}^2$ , which is correct, according to present knowledge, for temperatures  $\frac{1}{2} T_0$  or more below the transition temperature. Approaching the transition temperature  $T_0$ , it appears to increase like  $\lambda$  without limit.

(d) We now consider the field and current distribution in thin superconductors, i. e., those with thickness no longer great compared with the penetration depth. We first treat the example of a plane parallel slab extending from  $z = -d$  to  $z = +d$ . In the outside space let there be homogeneous magnetic fields  $\mathbf{H}^-$  where  $z < -d$  and  $\mathbf{H}^+$  where  $z > d$ , both in the  $y$  direction. The differential equation  $\Delta \mathbf{H} - \beta^2 \mathbf{H} = 0$  and the condition  $\operatorname{div} \mathbf{H} = 0$  are satisfied by

$$\mathbf{H}_x = \mathbf{H}_z = 0, \quad \mathbf{H}_y = a \cosh(\beta z) + b \sinh(\beta z) \quad (7-13)$$

It follows from eq. 7-1 that the current density is

$$\begin{aligned} i_y &= i_x = 0 & i_z &= -c \frac{\partial H_y}{\partial z} = -\lambda^{-1/2} \{a \sinh(\beta z) + b \cosh(\beta z)\} \end{aligned} \quad (7-14)$$



boundary condition that  $\mathbf{H}_y$  be continuous at  $z = \pm d$  yields two relations for the constants  $a$  and  $b$ :

$$h(\beta d) + b \sinh(\beta d) = H^+, \quad a \cosh(\beta d) - b \sinh(\beta d) = H^- \quad (7-15)$$

solution of these is

$$a = \frac{(H^+ + H^-)}{2 \cosh(\beta d)}, \quad b = \frac{(H^+ - H^-)}{2 \sinh(\beta d)} \quad (7-16)$$

$d \gg 1$  there exists a protected region free from field and current between two protecting layers of thickness  $1/\beta$ . If  $\beta d \ll 1$ , by expanding 7-13, 7-14, and 7-16 in series we find to a first approximation

$$i_y = \frac{1}{2} (H^+ + H^-) + \frac{1}{2} \frac{(H^+ - H^-)z}{d}, \quad i_x = c \frac{(H^- - H^+)}{2d} \quad (7-17)$$

face current density

$$i_x = 2d i_x = c(H^- - H^+)$$

before evenly distributed over the slab, the magnetic field increases with  $z$  if the field strengths differ on the two sides of the slab. However,  $H^+ = H^-$ , no current flows, and the field is constant. If in a homogeneous magnetic field we place a sufficiently thin superconducting sheet parallel to the field strength, the field penetrates the sheet it being disturbed. For arbitrary thickness, but with  $H^+ = H^-$ , 7-13 and 7-14 simplify to

$$\mathbf{H}_y = H^+ \frac{\cosh(\beta z)}{\cosh(\beta d)}, \quad i_x = -H^+ \frac{\sinh(\beta z)}{\sqrt{\lambda} \cosh(\beta d)} \quad (7-18)$$

Consider now the same slab with a surface current density  $i_x$  with magnetic field other than that produced by  $i_x$ . The current density is an even function of  $z$  as the positive and negative  $z$  directions are equivalent, and we therefore need those solutions of the fundamental 14 for which  $a = -b$ . Also by eq. 7-13  $\mathbf{H}_y$  is an odd function and consequently  $H^- = -H^+$ . Thus by eq. 7-15

$$b = \frac{H^+}{\sinh(\beta d)}$$

$$i_x = -H^+ \frac{\cosh(\beta z)}{\sqrt{\lambda} \sinh(\beta d)}, \quad \mathbf{H}_y = H^+ \frac{\sinh(\beta z)}{\sinh(\beta d)} \quad (7-19)$$

regard to the sign of  $i_x$ , it must be noticed that for the boundary surface the  $z$  direction is the outer normal, and not, as in eq. 7-10 the inner normal. cannot speak of the total current in this case because the slab is unlimited in the  $y$  direction.

## 7. STATIONARY FIELDS

Now we still have to calculate  $H^+$  from  $i_x$ . The equation

$$i_x = \int_{-d}^d i_x dz = -2cH^+ \quad (7-20)$$

will serve for this. So the final result reads

$$i_x = \frac{1}{2} \beta i_x \frac{\cosh(\beta z)}{\sinh(\beta d)}, \quad \mathbf{H}_y = -i_x \frac{\sinh(\beta z)}{2c \sinh(\beta d)} \quad (7-21)$$

For a thick slab ( $\beta d \gg 1$ ) one finds again that the field and current are concentrated in two protecting layers adjacent to the boundary surface. For thin sheets ( $\beta d \ll 1$ ), eq. 7-21 simplifies to

$$i_x = \frac{i_x}{2d}, \quad \mathbf{H}_y = \frac{i_x z}{2cd} \quad (7-22)$$

The current is therefore evenly distributed through the thickness of the sheet.

(f) To generalize the results obtained from these examples a mean value theorem for scalar space functions  $u$  that obey the differential equation  $\Delta u - \beta^2 u = 0$  (7-23) proves to be useful. We describe a sphere of radius  $r$  around an arbitrary point  $P$  in the three-dimensional domain of the function and form the mean value over its surface satisfying the equation

$$\Delta \bar{u} - \beta^2 \bar{u} = 0 \quad (7-24)$$

Since however  $\bar{u}$  depends only on  $r$

$$\Delta \bar{u} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{d\bar{u}}{dr} \right)$$

and the differential eq. 7-24 has the solutions

$$\bar{u} = \text{const.} \frac{\sinh(\beta r)}{\beta r} \quad \text{and} \quad \bar{u} = \text{const.} \frac{\cosh(\beta r)}{\beta r}$$

The second of these must be rejected because it increases without limit at  $r = 0$ . If we go to  $r = 0$  in the first one, we see that the constant must be  $u_P$ , therefore we find

$$u_P = \frac{\bar{u} \beta r}{\sinh(\beta r)} \quad (7-25)$$

The factor multiplying  $\bar{u}$  decreases from 1 to arbitrary small values with increasing  $r$ . For  $\beta = 0$  it would always be 1, and eq. 7-25 would go over into the well-known mean value theorem of potential theory, according to which the function  $u$  cannot have either a maximum or a minimum at any point  $P$ . However here, with  $\beta > 0$ , the equation says only that the absolute value  $|u_P|$  is smaller than the absolute value  $|\bar{u}|$ , excluding a maximum of  $|\bar{u}|$  at  $P$ , but certainly permitting a minimum. The highest values of  $|\bar{u}|$  never lie in the interior, but always on the boundary of the region in which the differential eq. 7-23 holds; for points on the surface it is not possible to construct such spheres so that eq. 7-25 does not apply.

The components  $\mathbf{H}_x$ ,  $\mathbf{H}_y$ , and  $\mathbf{H}_z$  of the magnetic field strength satisfy differential eq. 7-23; therefore we find according to this theorem that

$$(\mathbf{H}_x^2)_P < (\overline{\mathbf{H}_x^2})^2$$

wever, the mean square fluctuation over the surface of the sphere,

$$\frac{1}{4\pi r^2} \int (\mathbf{H}_x - \overline{\mathbf{H}_x})^2 |d\sigma| = \frac{1}{4\pi r^2} \int \mathbf{H}_x^2 |d\sigma| - (\overline{\mathbf{H}_x})^2 = (\overline{\mathbf{H}_x^2})^2$$

necessarily positive; therefore *a fortiori*

$$(\mathbf{H}_x^2)_P < \overline{\mathbf{H}_x^2}$$

ce corresponding relations hold for  $\mathbf{H}_y$  and  $\mathbf{H}_z$  we find by summation

$$(\mathbf{H}^2)_P < \overline{\mathbf{H}^2}$$

can prove in the same manner that

$$(\overline{\mathbf{H}^2})^2 < (\overline{\mathbf{H}^2})^2$$

re exists no maximum of the magnetic field strength or the current density in the interior of a superconductor. The highest values of  $\mathbf{H}^2$  and  $\mathbf{i}^2$  are always located at the surface. The possibility of minima is demonstrated by the examples in sections (d) and (e) and also by those in the following paragraphs. This is the general theory of the Meissner effect. If  $u$  depends only on two coordinates, the mean value is formed over the circle with radius  $r$  around the point  $P$ . Then

$$\Delta u = \frac{1}{r} \frac{d}{dr} \left( r \frac{du}{dr} \right)$$

eq. 7-25 is replaced by

$$u_P = \frac{\overline{u}}{I_0(i\beta r)} \quad (7-26)$$

re  $I_0(x)$  is the Bessel function of zero order to be discussed in more detail in Chap. 8. Since with increasing  $r$ ,  $I_0(i\beta r)$  increases continuously from 1 and finally exceeds all limits,<sup>8</sup> all conclusions drawn from eq. 7-25 be taken over in the two-dimensional case.

g) However, there are limits to be set to the Meissner effect which can be derived from eq. 7-25 or 7-26. If the region where the differential eq. 7-23 holds is small compared with the penetration depth  $\beta^{-1}$  then  $\beta^{-1} \gg 1$  and  $u_P = u$ , i. e., in such a region any solution of eq. 7-23 coincides with a solution of the potential equation  $\Delta u = 0$ . Then the Meissner effect becomes undetectable. Examples are contained in the following paragraphs 7-17 and 7-22 for the thin sheet; as a matter of fact in this case  $\mathbf{i}_P$  and  $\mathbf{H}_P$  do satisfy the potential equation.

in an infinitely long straight cylinder of arbitrary but small cross section its axis along the  $z$  direction, we can consider

$$\mathbf{i}_P = \text{constant}$$

<sup>8</sup>  $\epsilon = \sqrt{-1}$ .

Compare the series expansion of eq. 8-6.

as the first approximation, because in this way  $\Delta \mathbf{i}_P = 0$ . The supercurrent is then distributed in exactly the same way as an ohmic current. If, keeping the current density  $\mathbf{i}_P$  constant, we decrease all the dimensions of the cross section by a factor  $a$ , then the magnetic field strength decreases at corresponding points like  $a$  because by Stokes' theorem it follows from eq. II, for any surface lying entirely inside the conductor that

$$\int \mathbf{H} \cdot d\mathbf{s} = \frac{1}{c} \int \mathbf{i} \cdot d\mathbf{a}$$

and the surface of integration decreases like  $a^2$  while the circumference decreases like  $a$ . Equation IX shows that the ratio of curl  $\mathbf{i}$  to  $\mathbf{i}$  decreases like  $a$ . This justifies neglecting curl  $\mathbf{i}$  in eq. 7-23. We can take this result over without hesitation for a curved wire provided that the radius of curvature is great compared with the dimensions of the cross section.

On the other hand if we place a sufficiently small superconductor of arbitrary shape in a static magnetic field of strength  $H^0$ , then the field continues unchanged through the superconductor because it obeys the differential equation  $\Delta \mathbf{H} = 0$ . As here  $\mathbf{H}$  is curl free, no current is produced on this approximation. This is not a contradiction of eq. 7-5 because if we integrate that equation over a surface lying entirely inside the superconductor and transform the integral on the left side to a line integral over the circumference by means of Stokes' theorem we get

$$c \int \lambda \mathbf{i} \cdot d\mathbf{s} = - \int \mathbf{H} \cdot d\mathbf{o} \quad (7-28)$$

We apply this to two geometrically similar superconductors which may differ in their superconductivity constants  $\lambda_1$  and  $\lambda_2$ . Let  $L_1$  and  $L_2$  be corresponding linear intervals. We choose two corresponding surfaces in the superconductors; the integrals on the right-hand side of eq. 7-28 are then in the ratio  $(L_1/L_2)^2$ . Corresponding parts of the circumferences however are in the ratio  $L_1/L_2$ . Consequently the ratio of the current density components  $\mathbf{i}_\alpha$  at corresponding points of the two bodies is

$$\frac{\mathbf{i}_{\alpha 1}}{\mathbf{i}_{\alpha 2}} = \frac{\lambda_2 L_1}{\lambda_1 L_2} = \sqrt{\frac{\lambda_2}{\lambda_1}} \frac{\beta_1 L_1}{\beta_2 L_2}$$

Therefore for every sufficiently small superconductor every component  $\mathbf{i}_\alpha$  of  $\mathbf{i}$ ,  $\alpha = 1, 2, 3$ , can be developed in a series the first term of which has the form

$$\mathbf{i}_\alpha = H^0 \tau_\alpha \frac{\beta L}{\sqrt{\lambda}} \quad (7-29)$$

The quantities  $\tau_\alpha$  here are pure numbers, depending only on the relative positions and the shapes, but no longer on  $\lambda$  or the size of the specimen. Examples will be found in eqs. 10-2 and 11-12 as well as in the discussion following eq. 10-16.

These results do not hold without restriction for multiply connected superconductors because in this case there exist surfaces (see Chap. 12)

at extend partly outside the superconductor, in spite of the fact that air perimeters lie completely inside it. It is not then permissible to apply eq. 7-2 which is valid only for surfaces entirely within the superconductor. We shall see that in this case a persistent current, independent of  $H^0$ , can be superposed on the currents obeying eq. 7-29.

(h) According to Chap. 3 the constant  $\lambda$  is a function of temperature. Immediately below the transition temperature it is very great, and so is the penetration depth  $\beta^{-1} = c/\lambda$ . (See eq. 7-6.) Every specimen is then "small" in the sense of the present considerations, the magnetic field penetrates it undisturbed. With decreasing temperature  $\lambda$  decreases, at first very rapidly indeed. This initiates the expulsion of the field — the Meissner effect. If the specimen is wrapped with a normally conducting induction coil, one can follow this process by means of the induced current; decreases the flux of induction through the coil. Such experimentalists have often been carried out. In one instance Stark, Steiner, and Schoeneck<sup>9</sup> observed a "paramagnetic" effect in the induced current, i. e., effect that corresponds to an increase in flux of induction, which preceded the expulsion of the field. There is as yet no explanation for this. It would not help to ascribe to the superconductor a permeability  $\mu$  varying from 1. According to eq. 6-7 the former value  $1/c^2 \lambda$  of  $\beta^2$  merely acquires a factor  $\mu$ . As the observations concern  $\beta$ , this would change the conversion from  $\beta$  to  $\lambda$ , but would offer no explanation of the induction experiments.<sup>10</sup>

(i) We shall try to apply some of the above results to superconductors in noncubic crystal structure and consider again the simplest case: the superconductor fills half of space,  $x_3 > 0$ , and at its surface there is a static homogeneous magnetic field  $H^0$  the direction of which we again take the  $x_3$  axis. The boundary conditions for  $x_3 = 0$  are therefore

$$H_1 = 0, \quad H_2 = H^0 \quad (7-30)$$

or other boundary condition is again the gradual vanishing of all field vectors as  $x_3$  increases toward infinity. The Maxwell eq. II, ( $\text{curl } \mathbf{H} = \mathbf{H}/c$ )

<sup>9</sup> J. Stark, K. Steiner, and H. Schoeneck, *Phys. Z.*, **38**, 887 (1937).

<sup>10</sup> Another discrepancy with the theory appeared sometimes in such experiments that the total induced current impulse seemed to be less, occasionally even much less, than would be consistent with the complete expulsion of the field. The objection to these measurements is that the whole specimen had actually not become superconducting, but only a ring-shaped outer part of it. The cooling is effected from one side, so once such a ring is formed, it holds the enclosed flux of induction constant, as described in detail in Chap. 12, no matter how the external field is changed. The other parts remain in the intermediate state due to the influence of the field. In the superconducting ring a persistent current is produced by switching off the field, ap. 12). A test for this would consist in looking for the magnetic field of such a persistent current after the external field has been switched off, but it seems that this has never been made in such experiments.

and the London eq. X ( $c \text{ curl } \mathbf{G} = -\mathbf{H}$ ) reduce according to eq. VIII to the following:

$$i_1' = -c \frac{\partial H_2}{\partial x_3}, \quad i_2' = c \frac{\partial H_1}{\partial x_3} \quad (7-31)$$

$$\mathbf{H}_1 = c \left( \lambda_{21} \frac{\partial i_1'}{\partial x_3} + \lambda_{22} \frac{\partial i_2'}{\partial x_3} \right) \quad (7-32)$$

$$\mathbf{H}_2 = -c \frac{\partial G_1}{\partial x_3} = -c \left( \lambda_{11} \frac{\partial i_1'}{\partial x_3} + \lambda_{12} \frac{\partial i_2'}{\partial x_3} \right)$$

Because of the divergence conditions  $i_3'$  and  $H_3$  vanish. Elimination of  $\mathbf{H}$  leads to the differential equations

$$\begin{aligned} \lambda_{22} \frac{\partial^2 H_1}{\partial x_3^2} - \lambda_{21} \frac{\partial^2 H_2}{\partial x_3^2} - \frac{H_1}{c^2} &= 0 \\ -\lambda_{12} \frac{\partial^2 H_1}{\partial x_3^2} + \lambda_{11} \frac{\partial^2 H_2}{\partial x_3^2} - \frac{H_2}{c^2} &= 0 \end{aligned} \quad (7-33)$$

which here replaces eq. 7-6. The most obvious way to solve these is by introducing a new coordinate system  $x_1'$  and  $x_2'$  rotated about the  $x_3$  axis, in which the tensor component  $\lambda_{12}'$  vanishes. These are the "relative" principal axes of the tensor (i. e., relative to the plane  $x_3 = 0$ ), the principal axes of the ellipse formed by the intersection of this plane and the ellipsoid of the tensor:  $\sum \lambda_{\alpha\beta} x_\alpha x_\beta = \text{constant}$ . This ellipse gives the

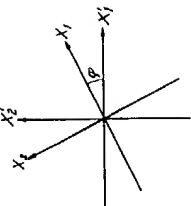


Fig. 7-1. Illustrating transformation of coordinates to principal axes.

"relative" principal values"  $\Lambda_1'$  and  $\Lambda_2'$  of the tensor. Introducing these changes in eq. 7-33 yields at once the two solutions:

$$(1) \quad H_1' = H_1^0 e^{-\beta_1' x_3}, \quad H_2' = 0 \quad (\beta_2' = 1/c \sqrt{\Lambda_2'})$$

$$i_1' = 0, \quad i_2' = -H_1^0 e^{-\beta_1' x_3} / \Lambda_2', \quad G_1' = -\sqrt{\Lambda_2'} H_1^0 e^{-\beta_1' x_3} \quad (7-34)$$

$$(2) \quad H_1' = 0, \quad H_2' = H_2^0 e^{-\beta_2' x_3}, \quad i_1' = 0, \quad G_1' = \sqrt{\Lambda_1'} H_2^0 e^{-\beta_2' x_3}, \quad i_2' = 0, \quad G_2' = 0 \quad (\beta_1' = 1/c \sqrt{\Lambda_1'}) \quad (7-35)$$

The integration constants  $H_1^0$  and  $H_2^0$  are the external magnetic field strength components in the directions  $x_1'$  and  $x_2'$  respectively. However, the boundary condition 7-30 must hold with respect to the coordinates  $x_1$  and  $x_2$ . Denoting the angle between  $x_1$  and  $x_1'$  by  $\varphi$ , as in Fig. 7-1, we have to put  $H_2^0 = H^0 \cos \varphi$ ;  $H_1^0 = -H^0 \sin \varphi$ . Finally transforming the vector components of eqs. 7-34 and 7-35 back into the components with respect to  $x_1$  and  $x_2$ ,

$$\mathbf{H}_1 = \mathbf{H}_1' \cos \varphi + \mathbf{H}_2' \sin \varphi, \quad \mathbf{H}_2 = -\mathbf{H}_1' \sin \varphi + \mathbf{H}_2' \cos \varphi, \text{ etc.}$$

and we find

$$\begin{aligned}
H_1 &= H^0 \{ e^{-\beta_1' x_1} - e^{-\beta_1' x_2} \} \cos \varphi \sin \varphi \\
H_2 &= H^0 \{ e^{-\beta_1' x_1} \cos^2 \varphi + e^{-\beta_1' x_2} \sin^2 \varphi \} \\
i_1^z &= H^0 \{ (1/\sqrt{A_1}) e^{-\beta_1' x_1} \cos^2 \varphi + (1/\sqrt{A_2}) e^{-\beta_1' x_2} \sin^2 \varphi \} \\
i_2^z &= -H^0 \{ (1/\sqrt{A_1}) e^{-\beta_1' x_1} - (1/\sqrt{A_2}) e^{-\beta_1' x_2} \} \cos \varphi \sin \varphi \\
G_1 &= H^0 \{ \sqrt{A_1} e^{-\beta_1' x_1} \cos^2 \varphi + \sqrt{A_2} e^{-\beta_1' x_2} \sin^2 \varphi \} \\
G_2 &= -H^0 \{ \sqrt{A_1} e^{-\beta_1' x_1} - \sqrt{A_2} e^{-\beta_1' x_2} \} \cos \varphi \sin \varphi
\end{aligned} \quad (7-36)$$

ording to Chap. 3 (b), the relative principal values  $A_1'$ ,  $A_2'$  are positive, before the decay constants  $\beta_1'$  and  $\beta_2'$  are certainly real. Because of boundary condition at infinity, we must take them to be positive. According to this, a noncubic crystal superconductor in a magnetic field also has a protecting layer under which exists a field-free region. contrast to the case with a scalar  $\lambda$ , the decay does not follow one ontential function but two. Furthermore, the magnetic field strength the protecting layer does not have the same direction  $x_2$  everywhere, in the outside space, nor does the current density have the same ction  $x_1$  everywhere perpendicular to this. Neither does the scalar uct ( $\mathbf{i} \cdot \mathbf{H}$ ) vanish. However, the two parts of the energy density, due to the supercurrent and that due to the magnetic field, remain il to each other, because from eq. 7-36

$$\frac{1}{2} (\mathbf{i} \cdot \mathbf{G}) = \frac{1}{2} H_0^2 \quad (7-37)$$

the total surface current  $\int_0^\infty \mathbf{i} dx_3$  flows perpendicular to  $H^0$  and alue is defined exclusively by  $H^0$  through eq. 7-36:

$$\int_0^\infty i_1^z dx_3 = c H^0, \quad \int_0^\infty i_2^z dx_3 = 0 \quad (7-38)$$

can of course be deduced directly from the Maxwell equations. All these differences vanish either if the relative principal values  $A_1'$ ,  $A_2'$  are equal, or if the external field coincides in direction with one e relative principal axes, i. e., if  $\varphi = 0$  or  $\pi/2$ . Then we return to of the solutions 7-34 or 7-35.

ne might also apply this solution to slightly curved conductors in so is they are thick compared with the penetration depths  $(\beta_1')^{-1}$  and  $(\beta_2')^{-1}$ , by considering the respective tangent planes as the  $x_3$  plane. or thin superconductors, however, the conditions are different. We easily from eq. 7-33 that for a sufficiently thin plate the external etic field penetrates without hindrance and that a supercurrent is y distributed over it. From this we infer that the conclusions drawn for thin cubic crystal superconductors may also be applied to other es. As a confirmation of this we find in Chap. 8 (e) and Chap. 11 (f), the solutions of London's equations, which lead to the above con- ns for cubic crystal cylinders and spheres, can under suitable conditions plied to other crystal lattice forms.

$t_3$  is generally not zero but  $t_3 = \lambda_{31} i_1^z + \lambda_{32} i_2^z$ .

## CHAPTER 8

## The Current Flowing in a Wire

(a) In sections (a) to (d) we shall discuss a circular cylinder of radius  $R$  carrying a current  $I$  in the direction of its axis, the  $z$  axis. We assume the current to be confined to a coaxial cylindrical shell so that we shall have a well-defined axially symmetrical external field. We assume the material of the superconductor to have a homogeneous cubic crystalline structure. We use cylindrical coordinates, the distance  $r$  from the axis, the azimuth angle  $\theta$  measured from an arbitrary direction, forming a right-handed system with  $z$  in the order  $r, \theta, z$  (compare Fig. 8-1). In these coordinates the components of the vector curl are

$$\text{curl}_r \mathbf{A} = \frac{1}{r} \frac{\partial A_z}{\partial \theta} - \frac{\partial A_\theta}{\partial z}$$

$$\text{curl}_\theta \mathbf{A} = \frac{\partial A_r}{\partial z} - \frac{\partial A_z}{\partial r} \quad (8-1)$$

$$\text{curl}_z \mathbf{A} = \frac{1}{r} \frac{\partial(r A_\theta)}{\partial r} - \frac{1}{r} \frac{\partial A_r}{\partial \theta}$$

and for a scalar  $u$ :

$$\Delta u = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 u}{\partial \theta^2} + \frac{\partial^2 u}{\partial z^2} \quad (8-2)$$

In what follows we shall use solutions of the differential equation  $\Delta u - \beta^2 u = 0$  of the form

$$u = f(r) e^{n\theta} e^{\pm k z} \quad (n \text{ an integer}) \quad (8-3)$$

Then  $f(r)$  must satisfy the equation

$$\frac{1}{r} \frac{d}{dr} \left( r \frac{df}{dr} \right) + \left( k^2 - \beta^2 - \frac{n^2}{r^2} \right) f = 0 \quad (8-4)$$

By the substitution  $x = \sqrt{k^2 - \beta^2} r$  this is transformed into the Bessel equation

$$\frac{1}{x} \frac{d}{dx} \left( x \frac{df}{dx} \right) + \left( 1 - \frac{n^2}{x^2} \right) f = 0 \quad (8-5)$$

The solutions of eq. 8-5 which remain finite for  $x = 0$  are the Bessel functions  $I_n(x)$ , namely,



Fig. 8-1. Cylindrical coordinates  $r, \theta$  for a wire. The  $z$  axis is directed toward the reader;  $A$  is the intersection of the  $z$  axis with the plane of the diagram.

$$\begin{aligned}
I_0(x) &= 1 - \frac{(\frac{1}{2}x)^2}{(1!)^2} + \frac{(\frac{1}{2}x)^4}{(2!)^2} - \dots + \frac{(-1)^m (\frac{1}{2}x)^{2m}}{(m!)^2} \dots \\
I_1(x) &= \frac{\frac{1}{2}x}{0!1!} - \frac{(\frac{1}{2}x)^3}{1!2!} + \frac{(\frac{1}{2}x)^5}{2!3!} - \dots + \frac{(-1)^m (\frac{1}{2}x)^{2m+1}}{m!(m+1)!} \dots \\
I_2(x) &= \frac{(\frac{1}{2}x)^2}{0!2!} - \frac{(\frac{1}{2}x)^4}{1!3!} + \frac{(\frac{1}{2}x)^6}{2!4!} - \dots + \frac{(-1)^m (\frac{1}{2}x)^{2m}}{(m-1)!(m+1)!} \dots
\end{aligned} \quad (8-6)$$

may verify that these series satisfy the following equations:

$$\begin{aligned}
\frac{dI_0(x)}{dx} &= -I_1(x) \\
\frac{dI_1(x)}{dx} &= I_0(x) - \frac{1}{x} I_1(x) \\
\frac{1}{x} \frac{d[x I_1(x)]}{dx} &= I_0(x) \\
\int_0^x I_0(\xi) d\xi &= x I_1(x) \\
\int_0^x \xi^2 I_1(\xi) d\xi &= x^2 I_2(x) \\
I_0(x) + I_2(x) &= \frac{2}{x} I_1(x)
\end{aligned} \quad (8-7)$$

real arguments,  $x$ , the functions  $I_n(x)$  oscillate about zero and have an infinity of roots. For pure imaginary arguments, the functions increase monotonically without limit with increasing argument.

1) Let us consider an infinitely long homogeneous superconducting cylinder. By symmetry the current density is parallel to the axis depends only on  $r$ . Therefore  $I_n$  must obey the differential eq. 8-4  $\pi = 0$  and  $k = 0$ . The substitution used in the transition to 1-5 is now  $x = i\beta r$  and so

$i_n = C I_0(i\beta r)$ ,  $i_z = i_0 = 0$  (8-8)  
 integration constant is determined by the condition that a total current  $i_s$  through the cross section. Consequently,

$$I = 2\pi \int_0^R r i_z dr = 2\pi C \int_0^R r I_0(i\beta r) dr = 2\pi \frac{CR}{\beta} [-i I_1(i\beta R)]$$

eq. 8-7). From this it follows that

$$C = \frac{(I i\beta/2\pi R)}{I_1(i\beta R)}, \quad i_z = \frac{i\beta I}{2\pi R} \frac{I_0(i\beta r)}{I_1(i\beta R)} \quad (8-9)$$

: according to eq. 8-6  $I_0(i\beta r)$  is real and positive, while  $I_1(i\beta r)$  is pure imaginary, the right sides of these equations are positive real. The magnetic field strength is determined by the fundamental eq. X:

$$\mathbf{H} = -c \lambda \operatorname{curl} \mathbf{i}$$

sof according to eq. 8-1

$$\mathbf{H}_r = \mathbf{H}_z = 0, \quad \mathbf{H}_\theta = c \lambda \frac{\partial i_z}{\partial r} = i c \lambda \beta C \left( \frac{dI_0(x)}{dx} \right)_{x=i\beta r} \quad (8-10)$$

$$\mathbf{H}_\theta = \sqrt{\lambda C} [-i I_1(i\beta r)] = \frac{I}{2\pi c R} \frac{I_1(i\beta r)}{I_1(i\beta R)} \quad (8-11)$$

We can check this equation by setting  $r = R$ . At the surface of the cylinder carrying a total current  $I$  we must have

$$\mathbf{H}_\theta = \frac{I}{2\pi c R} \quad (8-12)$$

and this actually is the result.

The Bessel functions  $I_0(i\beta x)$  and  $I_1(i\beta x)$  increase toward infinity as  $e^{i\beta x}/x$ . If  $\beta R$  is a high number, the wire therefore thick compared with the penetration depth, then according to eq. 8-9 with  $\beta r \gg 1$ ,  $i_z$  contains the factor  $e^{-\beta(r-R)}$ . The current, and likewise the magnetic field, lie almost entirely in a protecting layer of thickness  $\beta^{-1}$ . On the other hand  $I_0(i\beta x)$  has a minimum at  $x = 0$  (equal to 1), and if  $\beta R \ll 1$ , then the current density  $i_z$  increases only slightly from the axis to the perimeter — it is more or less evenly distributed over the section. Both results were to have been expected according to Chap. 7.

(c) Now let the cylinder consist of a normally conducting part where  $z < 0$  and a superconducting part where  $z > 0$ . According to Chap. 7 the electrostatic potential is constant inside the superconductor. The boundary plane at  $z = 0$  is thus an equipotential surface for the normal conductor; therefore the current flows exactly as in a wire of unlimited length, namely, it is evenly distributed over the cross section. The current density is

$$i_z = \frac{I}{\pi R^2} \quad (z < 0)$$

The magnetic lines of force here are circles around the axis of the wire. Since  $\int \mathbf{H}_\theta \cdot d\mathbf{s}$  integrated round a circle of radius  $r < R$  must equal the total current through the circle,  $I r^2/R^2$ , divided by  $c$ , we have

$$\mathbf{H}_\theta = \frac{r \cdot I}{2\pi c R^2} \quad (z < 0) \quad (8-13)$$

On entering the superconductor the current must restrict itself to the boundary layers. We have therefore to take into account a radial component  $i_r$  in the neighborhood of the boundary plane. Because of this it is more expedient to start with the magnetic field strength which even at this point has by symmetry only a component  $H_\theta$  independent of  $\theta$ . For large positive values of  $z$  we can use the solution 8-11 directly; in the neighborhood of  $z = 0$ , however, other terms have to be added that decrease with increasing  $z$ .

As already mentioned, the differential equation  $\Delta u - \beta^2 u = 0$  holds for  $H_r$  and  $H_z$ , but not for  $H_\theta$  which is associated with a curvilinear coordinate. Since, however,

$$\mathbf{H}_z = -\mathbf{H}_\theta \sin \theta, \quad \mathbf{H}_y = \mathbf{H}_\theta \cos \theta$$

we may write, using an a priori undetermined constant  $a_p$

$$\mathbf{H}_\theta = f(r) e^{-\sqrt{a_p^2 + \beta^2 z}}$$

so that we get

$$\mathbf{H}_y - i \mathbf{H}_z = f(r) e^{\beta z} e^{-\sqrt{a_p^2 + \beta^2 z}}$$

comparison with eq. 8-3 proves that  $f(r)$  must be a solution of eq. 8-4 with  $n = 1$  and  $k = \sqrt{\alpha_p^2 + \beta^2}$ , i. e.,

$$f(r) = I_1(\alpha_p r)$$

we insert such additional terms in the solution 8-11 it becomes consistent with eq. 8-12, an equation which must still hold; we therefore ermine  $\alpha_p$  by the requirement that

$$I_1(\alpha_p R) = 0 \quad (8-14)$$

there are infinitely many zeros of  $I_1(x)$ , a discrete but infinite set of  $\alpha_p$  values satisfy this condition.

In this way we arrive at the following series for  $H_\theta$ :

$$H_\theta = \frac{I}{2\pi c R} \left[ \frac{I_1(\beta R)}{I_1(\beta R)} + \sum_{p=1}^{\infty} \alpha_p I_1(\alpha_p r) e^{-\sqrt{\alpha_p^2 + \beta^2} z} \right] \quad (z > 0) \quad (8-15)$$

now have only the coefficients  $\alpha_p$  to calculate. For this purpose the continuity condition for  $H_\theta$  at  $z = 0$  is available. Because of eq. 8-13

$$\sum_{p=1}^{\infty} \alpha_p I_1(\alpha_p r) = \frac{r}{R} - \frac{I_1(\beta r)}{I_1(\beta R)} \quad (8-16)$$

it hold identically in  $r$ . To carry out the calculations two relations are table which we accept without proof:

$$\int_0^R r I_1(\gamma r) I_1(\delta r) dr = \frac{[\delta R I_1(\gamma R) I_0(\delta R) - \gamma R I_1(\delta R) I_0(\gamma R)]}{(\gamma^2 - \delta^2)} \quad (8-17)$$

the first of these follows the important fact that the functions  $I_1(\alpha_p r)$  ted by eq. 8-14 form an orthogonal system, i. e.,

$$\int_0^R r I_1(\alpha_p r) I_1(\alpha_q r) dr = 0 \quad \text{for } \alpha_p \neq \alpha_q$$

implying eq. 8-16 by  $r I_1(\alpha_q r)$  and integrating from 0 to  $R$  therefore nates all the coefficients except  $\alpha_q$  and yields for it the value

$$\alpha_q = \frac{\int_0^R r \left[ \frac{r}{R} - \frac{I_1(\beta r)}{I_1(\beta R)} \right] I_1(\alpha_q r) dr}{\int_0^R r I_1^2(\alpha_q r) dr}$$

Integration can be carried out easily by means of eqs. 8-7 and 8-17. result is

$$\alpha_q = -\frac{1}{2\alpha_q R} \left\{ \frac{I_0(\alpha_q R)}{I_0(\alpha_q R)} + \frac{\alpha_q^2 (\alpha_q^2 + \beta^2)}{I_2(\alpha_q R)} \right\}$$

Because of the last of the equations 8-7, eq. 8-14 is  $I_2(\alpha_q R) = -I_0(\alpha_q R)$  so

$$\alpha_q = -\frac{1}{2\alpha_q R} \frac{\beta^2 (\alpha_q^2 + \beta^2)}{I_0(\alpha_q R)} \quad (8-18)$$

We get the current density now from the fundamental eq. II:

$$\mathbf{i} = c \operatorname{curl} \mathbf{H}$$

According to eqs. 8-1, 8-7, and 8-15 this yields

$$\begin{aligned} i_z &= -c \frac{\partial H_\theta}{\partial z} = \frac{I}{2\pi R} \sum_{p=1}^{\infty} \alpha_p \left[ \frac{I_1(\alpha_p r)}{I_1(\alpha_p R)} e^{-\sqrt{\alpha_p^2 + \beta^2} z} \right] \\ i_r &= \frac{c}{r} \frac{d(r H_\theta)}{dr} \\ &= \frac{I}{2\pi R} \left[ \frac{\beta I_0(\beta r)}{I_1(\beta R)} + \sum_{p=1}^{\infty} \alpha_p I_0(\alpha_p r) e^{-\sqrt{\alpha_p^2 + \beta^2} z} \right] \\ i_\theta &= 0 \end{aligned} \quad (8-19)$$

Because of eq. 8-14  $i_r$  vanishes at the surface of the cylinder  $r = R$  as required. The same is true at  $r = 0$  because  $I_1(0) = 0$ .

Furthermore, as soon as  $\beta z \gg 1$ , both  $i_r$  and that part of  $i_z$  represented by the sum over  $p$  vanish. Then  $i_z$  assumes the same value as for the infinitely long superconducting cylinder given in eq. 8-9. The transition from the even current distribution that still exists at the boundary  $z = 0$  to the distribution that characterizes the superconductor is effected in a distance  $\beta^{-1}$ .

The first roots of eq. 8-14 are

$$\alpha_1 R = 3.83, \quad \alpha_2 R = 7.02, \quad \alpha_3 R = 10.2, \quad \alpha_4 R = 16.6 \dots$$

If therefore  $\beta R \geq 100$  (with  $\beta = 10^5 \text{ cm}^{-1}$ ,  $R = 10^{-3} \text{ cm}$  is sufficient for this), these first  $\alpha_p$  are all small compared with  $\beta$ . Then  $i_r$  is great compared with the contribution to  $i_z$  from the sum over  $p$ . But according to what has been said in section (b) about the exponential decay of the first terms, this contribution to  $i_z$  is practically the only one in the region where  $r$  is considerably smaller than  $R$ . So in this region the lines of flow, which leave the boundary of the normal conductor evenly distributed and perpendicular to the boundary, bend sharply into the radial direction. They have to do this because the major portion of the current must be deflected from the interior of the wire into the protecting layer of thickness  $\beta^{-1}$  adjoining the cylinder's surface, and do this within a distance of  $\beta^{-1}$  in the  $z$  direction.

The thinner the wire the greater become the  $\alpha_p$  and if  $\beta R \ll 1$  they are considerably greater than  $\beta$ . According to eq. 8-18 the coefficients  $\alpha_q$  then all decrease, and with them the sum in eq. 8-19, and so also the radial

ent  $i_r$ . The latter is no longer needed because, according to (b) the current is uniformly distributed over the cross section even in the superconductor.

d) Let the cylinder now consist of two superconductors touching in plane  $z = 0$ . Let the poorer superconductor lie below this plane;  $z < 0$ , according to the smaller constant  $\lambda'$ , and therefore to the greater mutual penetration depth  $\beta'$ . By section (b) the current distribution ends on  $\beta$  so transition phenomena must now appear on both sides of boundary.

or  $z > 0$  we can retain the expression 8-15 with the values of  $a_p$  by eq. 8-14, and also the consequent eq. 8-19. For  $z < 0$  we write the analogous expression:

$$i_\theta' = \frac{I}{2\pi c R} \left\{ \frac{I_1(\iota\beta r)}{I_1(\iota\beta R)} + \sum_{p=1}^{\infty} a_p' I_1(a_p r) e^{+\sqrt{a_p'^2 + \beta'^2} z} \right\} \quad (z < 0) \quad (8-20)$$

resulting calculation of the current distribution differs from eq. 8-19 only in the sign of the exponents but also in the sign of the right-hand side of the equations for  $i_r$ . We have two boundary conditions to evaluate coefficients  $a_p$  and  $a_p'$ , first the continuity of  $H_\theta$  and second (see Chap. 3, -9)

$$\lambda i_r = \lambda' i_r'$$

ling to eq. 6-7 we can also write for this

$$\frac{i_r}{i_r'} = \frac{\beta^2}{\beta'^2} \quad (8-21)$$

second condition is fulfilled identically in  $r$  only if the corresponding elements in the two series for  $i_r$  and  $i_r'$  are in the ratio  $\beta^2/\beta'^2$ :

$$\frac{a_p}{a_p'} \sqrt{\frac{(\alpha_p^2 + \beta^2)}{(\alpha_p'^2 + \beta'^2)}} = -\frac{\beta^2}{\beta'^2}$$

$$a_p' = -a_p \left( \frac{\beta'}{\beta} \right)^2 \sqrt{\frac{(\alpha_p^2 + \beta^2)}{(\alpha_p'^2 + \beta'^2)}} \quad (8-22)$$

continuity of  $H_\theta$ , however, requires that

$$\sum_{p=1}^{\infty} (a_p - a_p') I_1(a_p r) = \frac{I_1(\iota\beta' r)}{I_1(\iota\beta' R)} - \frac{I_1(\iota\beta r)}{I_1(\iota\beta R)} \quad (8-23)$$

ally in  $r$ . Applying the method used in (b) we conclude:

$$a_p - a_p' = \frac{2\alpha_p}{R I_0(\alpha_p R)} \frac{\beta'^2 - \beta^2}{(\alpha_p^2 + \beta^2)(\alpha_p'^2 + \beta'^2)} \quad (8-24)$$

uation and 8-22 determine both  $a_p$  and  $a_p'$ . We see that if we  $\beta' = \beta$  all the  $a_p$  and the  $a_p'$  vanish, as indeed must be so. transformation from one current distribution to the other takes two layers adjoining the boundary plane  $z = 0$  of thickness  $\beta - 1$

and  $\beta - 1$  respectively. It is effected by radial currents in both superconductors. To find the contributions of each of the two conductors, we compare the integrals  $\int_0^\infty i_r dz$  and  $\int_0^\infty i_r' dz$ . As

$$i_r = -c \frac{\partial H_\theta}{\partial z}$$

both yield the same value for  $(H_\theta)_{z=0}$ . The greater absolute value of  $i_r$ , which according to eq. 8-21 occurs in the better superconductor, is compensated by the smaller depth of the boundary layer. In the three cases treated here the magnetic field outside the superconductor is known *a priori*. The solutions therefore come under the uniqueness theorem of Chap. 7 (a).

(c) The solutions of section (b), i. e., of the problem of the infinitely long cylinder carrying a current, can be applied to noncubic crystal superconductors only if one of the axes of the ellipsoid representing the tensor  $\lambda_{ij}$  coincides with the axis of the cylinder. We call this axis the  $x_3$  axis. If  $i_r$  has this direction everywhere then by eq. VIII the supermomentum has only one component  $G_3$ . The only tensor component that enters the calculation is the principal value  $\lambda_3$ . It is only necessary to replace  $\beta$  in eqs. 8-9 and 8-10 by

$$\beta_3 = \frac{1}{c\sqrt{\lambda_3}} \quad (8-25)$$

to take over the former solution. Its uniqueness is again guaranteed by the theorem of Chap. 7 (a).

(f) It has not yet been possible to give a rigorous solution of our problem for a cylinder with an elliptical cross section, except in the approximation corresponding to the "thick" cylinder. In this case the circumference of the surface is a line of force of the external magnetic field. This field is irrotational and its potential obeys the equation  $\Delta\phi = 0$ , but it increases with each turn around the cylinder by the "period"

$$-\oint \mathbf{H} \cdot d\mathbf{s} = -\frac{I}{c}$$

where, as before,  $I$  means the total current in the cylinder. Let the axes of the elliptical cross section be  $a$  and  $b$  ( $a > b$ ). The "thick" cylinder is characterized by the fact that the smallest radius of curvature  $\beta/a$  at the ends of the greater axis is great compared with the penetration depth  $\beta - 1$ . The same holds *a fortiori* for  $b$ .

It is well known that if a functional relation  $\zeta = f(\chi)$  exists between two complex variables  $\zeta = x + iy$  and  $\chi = \psi + i\varphi$ , then  $\psi$  and  $\varphi$  are solutions of the potential equation. In the present problem

$\zeta = C \cosh(a\chi) = C [\cosh(a\psi) \cos(a\varphi) + i \sinh(a\psi) \sin(a\varphi)] \quad (8-26)$  can be adjusted to the given boundary conditions. The constants  $C$  and  $a$  are available for this purpose.

us it follows from eq. 8-26 that

$$x = C \cosh(\alpha\psi) \cos(\alpha\varphi), \quad y = C \sinh(\alpha\psi) \sin(\alpha\varphi) \quad (8-27)$$

ation of  $\varphi$  yields

$$\left[ \frac{x}{\cosh(\alpha\psi)} \right]^2 + \left[ \frac{y}{\sinh(\alpha\psi)} \right]^2 = C^2 \quad (8-28)$$

curves  $\psi = \text{constant}$  are everywhere orthogonal to the curves  $\varphi = \text{constant}$  and so represent the lines of force. If we fix a value  $\psi_0$  in way that

$$a = C \cosh(\alpha\psi_0) \quad \text{and} \quad b = C \sinh(\alpha\psi_0)$$

$$C^2 = a^2 - b^2, \quad \tanh(\alpha\psi_0) = \frac{b}{a} \quad (8-29)$$

the surface of the cylinder contains the corresponding line of force, defined by the one boundary condition. All the other lines of force pass confocal with the cross section of the cylinder. The period of potential has the prescribed value if we put

$$a = -\frac{2\pi c}{I} \quad (8-30)$$

magnitude  $H$  of the field strength follows from the general equation

$$H = |d\chi/dz|$$

ing to eq. 8-26:

$$H = \frac{1}{C} \frac{1}{|a| |\sinh(\alpha\chi)|} = \frac{1}{\{C|a| [\sinh^2(\alpha\psi) \cos^2(\alpha\varphi) + \cosh^2(\alpha\psi) \sin^2(\alpha\varphi)]^{1/2}\}} \quad (8-31)$$

icular the field strength at the surface  $\psi = \psi_0$  is (see eq. 8-29)

$$H^0 = \frac{I}{2\pi c} [a^2 \sin^2(\alpha\varphi) + b^2 \cos^2(\alpha\varphi)]^{-1/2} \quad (8-32)$$

ently at the end point of the greater axis ( $y = 0$ ,  $\sin(\alpha\varphi) = 0$  3-27),  $H^0$  is a maximum exceeding the minimum at the end of

transformation from  $\varphi$  to the polar angle  $\theta = \arctan y/x$  can be effected by ion following from eq. 8-27:

$$\tan \theta = \tanh(\alpha\psi) \tan(\alpha\varphi)$$

this to eq. 8-32 we have to put  $\tan \theta = (b/a) \tan(\alpha\varphi)$  according to The result is

$$H^0 = \frac{I}{2\pi c} \sqrt{\frac{a^2 \sin^2 \theta + b^2 \cos^2 \theta}{a^4 \sin^2 \theta + b^4 \cos^2 \theta}}$$

the smaller axis [ $x = 0$  and  $\cos(\alpha\varphi) = 0$ ] by the factor  $a/b$ . According to eq. 7-38 this statement is equally true of the surface density of the supercurrent, whatever the crystal structure of the conductor. If  $d$  is the perpendicular distance of an interior point from the surface, then according to eq. 7-10 for a cubic lattice, the current density within the protecting layer is

$$i_r = H^0 \lambda^{-1/2} e^{-\beta d} \quad (8-33)$$

and practically no current is flowing in the protected region beneath.

(g) The fact that the supercurrent prefers protruding edges is no peculiarity of the elliptical cylinder, but a general characteristic of this current. It is caused by the well-known fact that when the lines of force envelope the surface of a body, the field intensity is considerably increased at such edges. The potential theory proves this as follows.

If as in section (f) we start from the conformal mapping  $\chi = -iC\zeta^n$  then  $\psi$ , the real part of  $\chi$ , equals  $C|\zeta|^n \sin(n\theta)$ ; we take  $n$  to be a fraction between  $1/2$  and 1. The line of force  $\psi = 0$  consists of the radial lines  $\theta = 0$  and  $\theta = \pi/n$ . In our mapping we see the representation of a field whose lines of force run along the surface of the superconductor filling the space  $\pi/n < \theta < 2\pi$ . At the protruding edge  $\zeta = 0$

$$H = \left| \frac{d\chi}{d\zeta} \right| = nC|\zeta|^{n-1}$$

becomes infinite. If the edge is not mathematically sharp, but rounded,  $H$  remains finite, but in any case becomes especially large compared with the surrounding field. If we choose  $n > 1$  we get a re-entrant edge and see that  $H$  decreases to zero therein.

In a column with rectangular cross section the strongest current runs along the four edges.

However this holds only under the conditions for a "thick" superconductor, and this excludes mean radii of curvature comparable with or smaller than the penetration depth  $\beta^{-1}$ . In extremely thin superconductors the supercurrent is distributed evenly over the cross section in accordance with Chap. 7 (g).



$$\frac{dH_0(x)}{dx} = -H_1(x) \quad (9-4)$$

and is a solution of the differential eq. 8-5 with  $n = 1$ .  $H_1(\iota y)$  is negative real everywhere, becoming infinite like  $-2/(\pi y)$ ; it increases monotonically reaching the value zero only for infinitely large positive values of  $y$ . It now follows from eq. 8-3 as in eq. 8-10 that

$$H_0 = c\lambda \frac{\partial i_z}{\partial r} = \sqrt{\lambda} [C - \iota I_1(\iota\beta r) + D H_1(\iota\beta r)] \quad (9-5)$$

According to eqs. 9-1 and 9-2, the equations determining the constants  $C$  and  $D$  are

$$\begin{aligned} -\iota C I_1(\iota\beta R_i) + D H_1(\iota\beta R_i) &= \frac{\beta I'}{2\pi R_i} \\ -\iota C I_1(\iota\beta R_e) + D H_1(\iota\beta R_e) &= \frac{\beta(I + I')}{2\pi R_e} \end{aligned} \quad (9-6)$$

We need not write out the solution explicitly. For a thick hollow cylinder, i. e., when  $R_e - R_i \gg \beta^{-1}$ , the first terms in eqs. 9-3 and 9-5 decrease toward the interior and can be neglected completely in the neighborhood of  $R_i$ , and similarly the second terms decrease toward the outside and are negligible near  $R_e$ . Then we have simply

$$C = \frac{I_1(\iota\beta R_e)}{(I + I')(\iota\beta/2\pi R_i)}, \quad D = \frac{I'(\beta/2\pi R_i)}{H_1(\iota\beta R_i)} \quad (9-7)$$

Comparing this value of  $C$  with that in eq. 8-9 we see that the outer protecting layer of the cylindrical shell now carries the current  $I + I'$ . The equation for  $D$  shows that the protecting layer adjoining the inner surface carries the current  $-I'$ , because  $H_1(\iota\beta R_i)$  is negative and  $\iota H_0(\iota\beta r)$  in eq. 9-3 is positive. (See Fig. 9-1.) And this must be so; because a circle  $r = \text{constant}$  within the protected interior of the cylindrical shell must enclose zero net current because  $H = 0$  on the circle. This current  $-I'$  on the inner wall of the shell must be compensated by an additional current  $+I'$  in the outer surface in order to have the total current  $I$  for the whole cylinder. Also it is only in this way that we can satisfy at the inner wall the rule that the current, the magnetic field strength, and the inner normal to the superconductor form a right-handed system.

For thin hollow cylinders,  $R_e - R_i \ll \beta^{-1}$ , one develops the two cylinder functions of eq. 9-5 in powers of  $r - R_m$  starting from  $R_m = \frac{1}{2}(R_e + R_i)$ . One sees without calculation that, to a first approximation there is a linear transition from one to the other of the two values of  $H_0$  prescribed by eqs. 9-1 and 9-2. This corresponds to the linear transition in the thin plane parallel plate of Chap. 7, eq. 7-17.

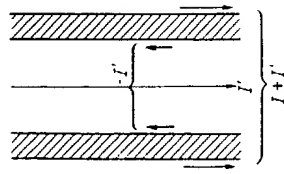


Fig. 9-1. Current distribution in a hollow superconducting cylinder with a coaxial wire.  $I$  is the net current in the superconducting cylinder;  $I'$  is the current in the coaxial wire.

## CHAPTER 9

### The Current Flowing in a Hollow Cylinder

a) For our present discussion let us consider a hollow cylinder with inner radius  $R_i$  and outer radius  $R_e$ . Let the cylinder be homogeneous, nonconducting, and have cubic crystal structure; let a total current  $I$  flow along it. But also let a wire, either normal or superconducting, be placed along the axis of the cylinder and carry another current  $I'$ . We consider  $I$  or  $I'$  to be positive if they flow in the positive  $z$  direction. We assume the circuit to be closed by means of a coaxial cylindrical shell at infinity, as in Chap. 8.

Under these circumstances the magnetic field strength at the inner cylindrical surface  $r = R_i$  is

$$H_0 = \frac{I'}{2\pi c R_i} \quad (r = R_i) \quad (9-1)$$

if a circle of radius  $R_i$  encloses the current  $I'$ . A circle lying in the cylindrical surface ( $r = R_e$ ), however, encloses the total current  $I'$ . Consequently the field strength there is

$$H_0 = \frac{I + I'}{2\pi c R_e} \quad (r = R_e) \quad (9-2)$$

Under these conditions we can obtain the fields within the cylinder uniquely according to the theorem of Chap. 7 (a).

The current is parallel to  $z$  and depends only on  $r$  just as for the solid cylinder (Chap. 8 (b)). Furthermore  $i_z$  is again a solution of the differential equation  $\Delta u - \beta^2 u = 0$ . But eq. 8-8 is insufficient because we cannot satisfy both conditions 9-1 and 9-2 with only one integration constant. However, we are relieved of the requirement that  $i_z$  must remain finite for  $r \rightarrow \infty$  because the domain of the desired solution does not extend so far. Therefore we can generalize the expression 8-8 as follows:

$$i_z = C I_0(\iota\beta r) + \iota D H_0(\iota\beta r) \quad (9-3)$$

$H_0(x)$  is the Hankel function of the first kind<sup>1</sup> and zero order, namely, a solution of the differential eq. 8-5 with  $n = 0$  which becomes logarithmically infinite at the origin;  $I_0(x)$  also satisfies eq. 8-5.  $H_0(x)$  is defined that  $\iota H_0(\iota y)$  is positive real for positive real  $y$  and behaves like  $-(2/\pi) \ln y$ ; it decreases monotonically with increasing  $y$ , finally vanishing asymptotically. The Hankel function of the first kind first order  $H_1(x)$  is connected with  $H_0(x)$  by the relation

<sup>1</sup> We can omit the usual superscript 1 because we shall not have to deal with the function of the second kind.

e solution given in eqs. 9-6 and 9-7 can be generalized to non-crystals as in Chap. 8 (d) if one principal axis of the tensor falls in the plane of the cylinder. One only has to replace  $\beta$  by the  $\beta_z$  of eq. 8-25. The thing that follows in this chapter holds independently of all crystalline properties.

explained in Chap. 1 every "thick" superconductor (there have been scarcely any experiments done on thin hollow cylinders) can stand only a certain critical value  $H_c$  at its surface. According to eqs. 9-1 and 9-2 this sets a limit for the superconducting state of the hollow cylinder:

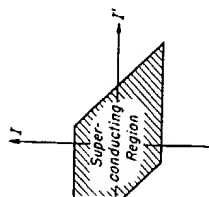
$$|I'| < 2\pi c R_i H_c, \quad |I + I'| < 2\pi c R_o H_c \quad (9-8)$$

If we plot  $I$  and  $I'$  as coordinates in a plane (Fig. 9-2) the interior of the shaded parallelogram represents the region of superconductivity. This simple consequence of the Silsbee hypothesis has never been checked experimentally in a rigorous manner.

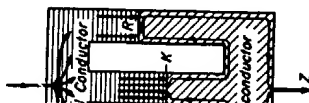
(b) Figure 9-3 represents the cross section of an arrangement of normal and superconducting parts symmetrical with respect to the  $z$  axis. Leads in the  $z$  axis may supply the current  $I$ . We ask what part of  $I$  flows through the inner solid cylinder, and what part flows through the outer hollow cylinder. This is decided not in the superconductor, but in the normal conductor. The circular sections  $K$  and the annular ring  $R$  in the figure have the same potential because the electrostatic potential in a superconductor is constant. Potential theory applied to the interior of the normal conductor then tells us what part of  $I$ , takes the path through the inner cylinder.

This current enters the superconductor at  $K$  and must finally reach the lower lead. As it cannot penetrate deeply into the superconductor, it can only go along the boundary of the superconductor, as sketched in the figure. It flows, in fact, across the plane  $R$  and there joins the current  $I - I'$  that enters the outer surface of the superconductor from above. The full current then flows down the outer surface to the lower leads.

The uniqueness of the solution sketched here is again guaranteed by the theorem of Chap. 7 (d). To begin with, owing to the symmetry of the arrangement, the magnetic field is known for all bounda-



2. Diagrammatic representation of Silsbee's hypothesis for a hollow superconducting cylinder;  $I$  is the net current entering the superconducting cylinder;  $I'$  is the current in the coaxial wire.



3. Current lines at the interface between normal and superconducting parts of a cylinder.

ries, e. g., the lower surface  $F$  of the superconductor. After solving the potential problem for the normal conductor (which is possible only in one way) our knowledge of  $I_1$  allows us to find the field distribution first in the hollow space between the inner cylinder and the outer shell, secondly at the boundaries  $K$  and  $R$  of the superconductor, and therefore at all surfaces of the latter.

(c) Figure 9-4 represents a similar arrangement only in this case the whole shaded area is to be superconducting. Again we imagine the current  $I$  to be fed in at  $Z$  and carried back by a third cylinder  $C_3$  coaxial with  $C_1$  and  $C_2$ . This shields the field from outside because a curve enclosing it encloses a net current zero. The circuit for the current  $I_1$  flowing in  $C_1$  is completed by the inner walls of  $C_2$  and the two superconducting caps. It does not affect the outside at all, so long as the superconducting parts are thick compared with the penetration depth, but neither can it be influenced from the outside. It is a persistent current in what is here actually a doubly connected body. Its energy is substantially of magnetic nature and is located in the hollow space between  $C_1$  and  $C_2$  and has the form  $a I_1^2$ ; the value of the constant  $a$  is of no importance.

One can also consider this apparatus from another point of view. The parts formed by sections at  $A$  and  $B$  can be regarded as superconductors in parallel in the sense of Chap. 2. In order to permit the current strength  $I_2$  in the cylinder  $C_2$  a current  $I_1 + I_2$  must flow along its outer walls because the inner wall carries the current  $-I_1$ . Consequently the energy located between  $C_2$  and  $C_3$  (and to an unimportant degree also in the protecting layer of  $C_3$ ) is of the form  $\gamma (I_1 + I_2)^2$ . Writing the total energy  $a I_1^2 + \gamma (I_1 + I_2)^2$  in the form  $\frac{1}{2} (p_{11} I_1^2 + p_{22} I_2^2 + 2 p_{12} I_1 I_2)$  we have  $p_{12} = \gamma p_{22} = 2\gamma$ . According to eq. 2-6 it follows that if there were no current in the system initially,  $I_1$  would remain zero after switching on the current  $I$ , while any initial current  $I_1$  would remain unchanged by switching on  $I$ .

These considerations, although leading to no new results, nevertheless show the intimate relations between the discussion of Chap. 2 and the theory explained in Chap. 3 and later chapters.

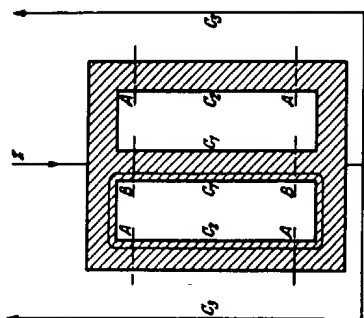


Fig. 9-4. Doubly connected superconductor in the same arrangement as in Fig. 9-3.

The requirements that  $\mathbf{H}_t$  goes over continuously into  $H_t$  at  $r = R_c$  and to  $H_t$  at  $r = R_i$  serve to determine the constants  $C$  and  $D$ .

If the walls of the cylinder are thick compared with  $\beta^{-1}$  we can in eq. 10-4 neglect the first term when  $r = R_i$  and the second term when  $r = R_c$ , as we did in Chap. 9 (a). We then have to put

$$C = \frac{H_i}{I_0(\iota\beta R_c)}, \quad D = \frac{H_i}{\iota H_0(\iota\beta R_i)} \quad (10-6)$$

This leads back to eq. 10-1 for the layer at the outer boundary, while for the neighborhood of the inner boundary it follows that

$$\mathbf{H}_t = H_i \frac{H_0(\iota\beta r)}{H_0(\iota\beta R_i)}, \quad i_\theta = -\frac{H_i}{\iota\sqrt{\lambda} H_0(\iota\beta R_i)} \frac{H_1(\iota\beta r)}{H_1(\iota\beta R_i)} \quad (10-7)$$

Since  $H_1(\iota\beta r)$  is negative while  $\iota H_0(\iota\beta R_i)$  is positive, the current for positive  $H_i$  has again the direction of increasing  $\theta$ . A field-free region is located between the two protective layers where these equations hold.

Let us choose  $H_c = 0$ . If we ascribe to the cylinder a finite length which, however, is great compared with its diameter, eqs. 10-7 are still valid except in the neighborhood of the ends. Here we have an example of a persistent current, because indeed a hollow cylinder is a doubly connected body.

Let us assume the cylinder to be thin ( $R_c - R_i \ll \beta^{-1}$ ) and choose  $H_c = H_i$ . Writing  $R_m$  for the arithmetic mean between  $R_c$  and  $R_i$ , the first terms of the expansion will now suffice:

$$\mathbf{H}_t = (\mathbf{H}_t)_{R_m} + \left( \frac{\partial \mathbf{H}_t}{\partial r} \right)_{R_m} (r - R_m)$$

If the right-hand side has to assume the same value,  $H_t$  at  $r = R_i$ , i. e., at  $r - R_m = -1/2(R_c - R_i)$ , as it does at  $r = R_c$ , i. e., at  $r - R_m = 1/2(R_c - R_i)$ , then  $(\partial \mathbf{H}_t / \partial r)_{R_m}$  must be zero; consequently according to eq. 10-5 (1)  $i_\theta$  is also zero. This again confirms the general argument of Chap. 7 (b) for thin specimens.

The solutions given in eqs. 10-1 and 10-2, 10-4 and 10-5 remain valid for noncubic crystals provided the ellipsoid of the tensor  $\lambda_{\alpha\beta}$  has an axis of symmetry (say  $x_3$ ) in the direction of the axis of the cylinder, and the two principal values  $\lambda_1$  and  $\lambda_2$  coincide. Then for this problem the supermomentum is in fact always in the same direction as the supercurrent, just as in the cubic case, while

$$\beta_1 = \frac{1}{c\sqrt{\lambda_1}} \quad (10-8)$$

replaces  $\beta$  in the calculation.

(c) Now let us imagine a solid cylinder of radius  $R$  with no longitudinal current, placed in a field perpendicular to its axis — a transverse field. The field does not remain homogeneous as the lines of force must go around the cylinder if the latter is not too thin, i. e., they are deflected by it as shown in Fig. 1-5. If we are not satisfied with the approximation used in the figure, which regards the superconductor as completely impenetrable to the field (a case for which the distortion of the field can easily be

## CHAPTER 10

### The Cylinder in a Homogeneous Magnetic Field

a) We now place a homogeneous superconducting cylinder in a longitudinal magnetic field; no current flows in the direction of its axis; the external field has where the same strength  $\mathbf{H}_t = H^0$  outside the surface of the cylinder. In the interior of the cylinder  $\mathbf{H}_t$  has to satisfy the equation  $\Delta u - \beta^2 u = 0$  must moreover depend only on the distance  $r$  from the axis. Like the current density  $i_\theta$  in Chap. 8 (b) which satisfied the same conditions,  $\mathbf{H}_t$  therefore be proportional to  $I_0(\iota\beta r)$ . The boundary condition that  $\mathbf{H}_t$  is continuous is then obviously satisfied by

$$\mathbf{H}_t = H^0 \frac{I_0(\iota\beta r)}{I_0(\iota\beta R)} \quad (10-1)$$

and the current density from  $\mathbf{i} = c \operatorname{curl} \mathbf{H}$ . According to eq. 8-1 we have:

$$i_\theta = i_\theta = 0, \quad i_\theta = -c \frac{\partial \mathbf{H}_t}{\partial r} = \iota H^0 \frac{I_1(\iota\beta r)}{\sqrt{\lambda} I_0(\iota\beta R)} \quad (10-2)$$

eq. 8-7  $dI_0(x)/dx = -I_1(x)$ . From the form of these two Bessel functions, discussed in Chap. 8 (b) it also follows here that the influence of the field on a thick wire is confined to a protecting layer of thickness  $\beta^{-1}$ . Currents that provide this protection flow in the direction of increasing  $\theta$  if  $H^0$  is positive because  $-I_1(\iota\beta r)$  is positive. This corresponds to the rule that current, field strength, and inner normal to the superconductor — here the negative  $r$  direction — form a right handed system. In thin wire ( $\beta R \ll 1$ ) the flat minimum of  $I_0(\iota\beta r)$  at  $r = 0$  shows the field penetrates almost without loss. In this case

$$i_\theta = -\frac{1}{2} \frac{H^0 \beta r}{\sqrt{\lambda}} \quad (10-3)$$

comes identical with eq. 7-29 if one puts  $L = R$  and  $\tau_a = -r/2R$ . Now let us consider a hollow cylinder with radii  $R_i$  and  $R_c$  having strength  $\mathbf{H}_t = H_i$  in the bore, whereas outside there is a homogeneous field  $\mathbf{H}_t = H_c$ . Within the superconductor  $\mathbf{H}_t$  has to satisfy the same differential equation as in case (a); but for the reasons we have discussed in p. 9 (c) in connection with the hollow cylinder carrying a current, we write down the analogous expression to eq. 9-3:

$$\mathbf{H}_t = C I_0(\iota\beta r) + \iota D H_0(\iota\beta r) \quad (10-4)$$

his it follows, as in (a) (compare also eq. 9-5) that

$$i_\theta = -c \frac{\partial \mathbf{H}_t}{\partial r} = \iota c \beta C I_1(\iota\beta r) - c \beta D H_1(\iota\beta r) \quad (10-5)$$

ulated by potential theory) we have to try to determine the internal the external field simultaneously. We come here for the first time to an principle in which the external field cannot be specified in advance. The uniqueness theorem of Chap. 7 (a) is no longer applicable; instead we shall use a more general uniqueness theorem worked out in Chap. 12 (d). We introduce rectangular coordinates in a plane perpendicular to the wire to supplement the polar coordinates  $r$  and  $\theta$  used hitherto:

$$x = r \cos \theta, \quad y = r \sin \theta$$

pose the intensity of the homogeneous field has the positive direction magnitude  $H^0$ . Its potential would then be

$$\phi = -H^0 x = -H^0 r \cos \theta$$

ording to potential theory a completely impenetrable cylinder would at points outside it as a dipole sheet, and its potential would be of the form  $(a/r) \cos \theta$ , with  $a = R^2$ . We therefore seek a rigorous solution to the problem in the following form with  $a$  at first undetermined:

$$\phi = -H^0 \left( r + \frac{a}{r} \right) \cos \theta \quad (10-9)$$

use  $\mathbf{H} = -\text{grad } \phi$  it follows that

$$H_r = -\frac{\partial \phi}{\partial r} = H^0 \left( 1 - \frac{a}{r^2} \right) \cos \theta$$

$$H_\theta = -\frac{1}{r} \frac{\partial \phi}{\partial \theta} = -H^0 \left( 1 + \frac{a}{r^2} \right) \sin \theta \quad (10-10)$$

see that eq. 10-10 yields  $H_r = 0$  for  $a = R^2$  and  $r = R$ , corresponding to the case of impenetrability.)

$\phi$  is therefore proportional to  $\sin \theta$  on the boundary as well as in the internal space. Remembering the intimate connection between the current density and the tangential component of magnetic field, which we first met when discussing thick specimens, it is natural to put inside the cylinder

$$i_r = i_\theta = 0, \quad i_z = f(r) \sin \theta \quad (10-11)$$

$i_z$  must be a solution of  $\Delta u - \beta^2 u = 0$ , the differential eq. 8-4 with  $k = 0$  and  $n = 1$  must be satisfied by  $f(r)$ . Furthermore  $f(r)$  must be finite and continuous at  $r = 0$  so that

$$f(r) = i C I_1(\epsilon \beta r), \quad i_z = i C I_1(\epsilon \beta r) \sin \theta \quad (10-12)$$

$C$  is an integration constant. From  $\mathbf{H} = -c \lambda \text{curl } \mathbf{i}$  and eq. 8-1 it follows therefore that

$$\begin{aligned} H_r &= -\frac{c \lambda}{r} \frac{\partial i_z}{\partial \theta} = -\frac{c \lambda C}{r} i I_1(\epsilon \beta r) \cos \theta \\ &= -\frac{\sqrt{\lambda} C}{\beta r} i I_1(\epsilon \beta r) \cos \theta \end{aligned} \quad (10-13)$$

$i \cos \theta$  is the real part of the function  $\zeta^{-1}$  of the complex variable  $\zeta = x + iy$  this way a solution of the potential equation.

and, noting one of the eqs. 8-7,

$$\mathbf{H}_\theta = c \lambda \frac{\partial i_z}{\partial r} = -\sqrt{\lambda} C [I_0(\epsilon \beta r) - \frac{1}{\epsilon \beta r} I_1(\epsilon \beta r)] \sin \theta \quad (10-14)$$

For boundary conditions we have the continuity of the two components of  $\mathbf{H}$  at  $r = R$ . These can be satisfied by the above expressions, and this justifies our chosen procedure. As a comparison of eqs. 10-13 and 10-14 with 10-10 shows, we have only to adjust the constants  $a$  and  $C$  so that

$$H^0 \left( 1 - \frac{a}{R^2} \right) = \frac{\sqrt{\lambda} C}{\epsilon \beta R} i I_1(\epsilon \beta R) \quad (10-15)$$

$$H^0 \left( 1 + \frac{a}{R^2} \right) = \sqrt{\lambda} C \left[ I_0(\epsilon \beta R) - \frac{1}{\epsilon \beta R} I_1(\epsilon \beta R) \right]$$

These requirements yield:

$$\begin{aligned} C &= \frac{H^0}{\sqrt{\lambda} I_0(\epsilon \beta R)}, \quad 1 - \frac{a}{R^2} = \frac{2}{\epsilon \beta R} \frac{I_1(\epsilon \beta R)}{I_0(\epsilon \beta R)} \\ i_z &= \frac{2 H^0 \sin \theta i I_1(\epsilon \beta r)}{\sqrt{\lambda} I_0(\epsilon \beta R)} \end{aligned} \quad (10-16)$$

According to eqs. 10-13 and 10-14 the magnetic lines of force in the interior of the cylinder must be such that  $i_z = \text{constant}$ . For thick cylinders this means

$$\frac{i I_1(\epsilon \beta r)}{I_0(\epsilon \beta R)} = -e^{-(R-r)} \quad (10-17)$$

The right-hand side of the equation for  $a$  becomes zero, and  $a$  assumes the potential theory value  $R^2$ , and at the surface, according to eq. 10-10 we shall have

$$(\mathbf{H}_\theta)_R = -2 H^0 \sin \theta$$

The maximum  $2 H^0$  of  $|\mathbf{H}_\theta|$  illustrates the doubling of the field strength due to field deformation discussed in Chap. 1 (g). From eqs. 10-16 and 10-17, however, it follows that

$$i_z = -2 H^0 \lambda^{-1/2} e^{-\beta(R-r)} \sin \theta = \lambda^{-1/2} (\mathbf{H}_\theta)_R e^{-\beta(R-r)}$$

The same result would be obtained from eq. 7-10 by adapting to a cylindrical surface the equation given there for a plane boundary. Such a step would be justified for a thick cylinder. The protecting layer obeys the same laws here as at a plane surface.  $i_z$  is negative for positive  $\theta$ , i. e., in the upper part of Fig. 1-5, so the current is flowing away from the reader; this fact corresponds to the general rule that current, magnetic field, and internal normal form a right-handed system.

According to eq. 10-17 and the equation for  $a$  in 10-16 we have, for a thick cylinder

$$a = R^2 \left( 1 - \frac{2}{\epsilon \beta R} \right)$$

magnetic moment is decreased by the factor  $(1 - 2/\beta R)$  compared with the case of a completely vanishing penetration depth ( $\beta \rightarrow \infty$ ). For cylinders ( $\beta R \ll 1$ ),  $I_0(\epsilon \beta R) = 1$  and  $I_1(\epsilon \beta R) = \frac{1}{2} \epsilon \beta R$ . Compare the series 8-6). The right-hand side of equation 10-16 for  $a$  now becomes equal to unity and  $a = 0$ . According to eq. 10-9 the field now straddles the cylinder without being deflected and no longer induces any current in it, because, according to eq. 10-16  $i_z$  vanishes like  $\beta R$  in agreement with eq. 7-29.

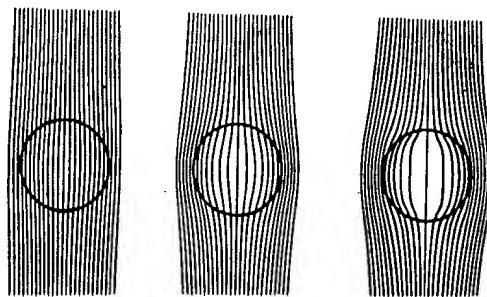
According to eq. 8-6 we have the following series expansions:

$$\begin{aligned} \frac{I_1(\epsilon x)}{I_2(\epsilon x)} &= 1 + \frac{(\frac{1}{2}x)^2}{1!2!} + \frac{(\frac{1}{2}x)^4}{2!3!} + \dots + \frac{(\frac{1}{2}x)^{2m}}{m!(m+1)!} + \dots \\ I_0(\epsilon x) &= 1 + \frac{(\frac{1}{2}x)^2}{(1!)^2} + \frac{(\frac{1}{2}x)^4}{(2!)^2} + \dots + \frac{(\frac{1}{2}x)^{2m}}{(m!)^2} + \dots \end{aligned}$$

In the second series the coefficients of all powers of  $x$  are greater than the corresponding coefficients in the first series, therefore  $I_0(\epsilon x) > 2I_1(\epsilon x)/\epsilon x$ , and it increases with increasing  $x$  more rapidly than  $2I_1(\epsilon x)/\epsilon x$ . The right-hand side of eq. 10-16 for  $a$  is therefore smaller than unity for all values of  $\beta R$  and continually decreases with increasing  $R$  but without becoming negative. Therefore  $a$  increases with increasing  $R$  monotonically from 0 to  $R^2$ , the limit already mentioned.

Figure 10-1 shows the form of the lines of force for three different values of  $\beta R$ . In the external space the lines follow the same course as with a diamagnetic specimen. However, whereas inside a diamagnetic body they would be straight, here they are more or less curved.

If the temperature is lowered, starting from the transition temperature, the penetration depth  $\beta^{-1} = c/\lambda$  is at first great, and so  $\beta R$  is a small number for any given value of  $R$ . Later  $\beta^{-1}$  decreases and  $\beta R$  increases. The figures represent in any the gradual expulsion of the field from the interior of the specimen. In the final phase,  $\beta R \gg 1$  is shown in Fig. 1-5.



10-1. Lines of force for a thin conducting cylinder in a transverse homogeneous magnetic field for different values of penetration depth.  $\epsilon = 1$ : a)  $\beta R = 2$ ; b)  $\beta R = 3$

As the current here has only one component  $i_z$ , the solution implied by eqs. 10-12, 10-13, and 10-14 can be taken over for noncubic crystals under the same conditions as set up in Chap. 8 (e).

(d) No rigorous solution can yet be given for an elliptical cylinder in an external field; just as was the case for the cylinder carrying a current treated in Chap. 8 (d), we must confine ourselves again to the approximation that holds only for "thick" cylinders. The boundary curve must then be a field line. The solution is trivial for the longitudinal field: everywhere in the external space the field strength  $H_z$  is constant and equal to  $H_0$ , and the current density can be calculated by eq. 7-10.

For the transverse field, however, we assume that the field strength forms an angle  $\theta_0 < \frac{1}{2}\pi$  with the  $a$  axis at a great distance from the cylinder. For the description of the field we use, as in Chap. 8 (e) a function of the complex variable  $\zeta = x + iy$ , which we shall call  $W = U + iV$ , and take  $U$  as the potential. We define  $W$  in terms of the complex parameter  $\chi = \psi + i\varphi$ , namely,

$$W = -\frac{1}{2} H_0 \sqrt{a^2 - b^2} \left( e^{-\chi - i\theta_0} + \frac{a+b}{a-b} e^{-\chi + i\theta_0} \right) \quad (10-18)$$

$$\zeta = \sqrt{a^2 - b^2} \cosh \chi$$

The second of these equations follows from eq. 8-26 by putting  $\alpha = 1$  there. In analogy to eq. 8-27 we have here

$$x = \sqrt{a^2 - b^2} \cosh \psi \cos \varphi, \quad y = \sqrt{a^2 - b^2} \sinh \psi \sin \varphi \quad (10-19)$$

and the curves  $\psi = \text{constant}$  are the confocal ellipses

$$\frac{x^2}{\cosh^2 \psi} + \frac{y^2}{\sinh^2 \psi} = a^2 - b^2 \quad (10-20)$$

Let the contour of the cylinder correspond to the value  $\psi_0$ , so that

$$\sqrt{a^2 - b^2} \cosh \psi_0 = a, \quad \sqrt{a^2 - b^2} \sinh \psi_0 = b$$

$$e^{\pm \psi_0} = \sqrt{\frac{a+b}{a-b}} \quad (10-21)$$

The curves  $\varphi = \text{constant}$ , however, are the hyperbolas confocal to these ellipses:

$$\frac{x^2}{\cosh^2 \varphi} - \frac{y^2}{\sinh^2 \varphi} = a^2 - b^2 \quad (10-22)$$

$\psi$  and  $\varphi$  are called elliptical coordinates. To make them single valued we restrict them to the ranges of values 0 to  $+\infty$  for  $\psi$  and 0 to  $2\pi$  for  $\varphi$ . Each of the above hyperbolas then corresponds to four  $\varphi$  values: if  $\varphi = \varphi_0$  is the semi-axis in the first quadrant ( $x > 0, y > 0$ ), then  $\varphi = \pi - \varphi_0$  is the semi-axis in the second quadrant ( $x < 0, y > 0$ ),  $\varphi = \pi + \varphi_0$  that in the third quadrant ( $x < 0, y < 0$ ) and  $\varphi = 2\pi - \varphi_0$  in the fourth ( $x > 0, y < 0$ ).

\*The assumption that  $\theta_0 > \frac{1}{2}\pi$  leads to nothing new.

from eq. 10-18 it follows that

$$\begin{aligned} U &= -\frac{1}{2} H^0 \left[ \frac{a^2}{a^2 - b^2} e^{\psi} + \frac{a+b}{a-b} e^{-\psi} \right] \cos(\varphi - \theta_0) \\ V &= -\frac{1}{2} H^0 \left[ \frac{a^2}{a^2 - b^2} e^{\psi} - \frac{a+b}{a-b} e^{-\psi} \right] \sin(\varphi - \theta_0) \end{aligned} \quad (10-23)$$

use of the way they were derived from eq. 10-18,  $U$  and  $V$  are solutions of a potential equation.  $\psi$  is infinite at infinity, according to eq. 10-19, before at infinity

$$U = -\frac{1}{2} H^0 \left[ \frac{a^2}{a^2 - b^2} e^{\psi} (\cos \varphi \cos \theta_0 + \sin \varphi \sin \theta_0) - H^0 (x \cos \theta_0 + y \sin \theta_0) \right]$$

field is therefore homogeneous at infinity, and inclined at an angle  $\theta_0$  to the  $x$  axis. The field line  $V = 0$  consists first of those parts of the circles  $\varphi = \theta_0$  and  $\varphi = \pi + \theta_0$  which lie outside the ellipse  $\psi_0$  (since formulas are valid outside), and secondly of the ellipse  $\psi_0$ ; because lying to eq. 10-21 on this ellipse

$$e^{\psi_0} = \frac{a+b}{a-b} e^{-\psi_0}$$

expression 10-18 thus satisfies all the imposed conditions. We proceed to the calculation of  $|\mathbf{H}| = |\mathbf{dW}/d\zeta|$ . From eq. 10-18

$$\begin{aligned} \frac{dW}{d\zeta} &= \frac{(\mathbf{dW}/d\zeta)}{(\mathbf{d}\zeta/d\chi)} = -\frac{H^0}{2 \sinh \chi} \left( e^{\chi - i\theta_0} - \frac{a+b}{a-b} e^{-\chi + i\theta_0} \right) \\ &= H^0 \left[ \frac{a+b}{a-b} e^{-\chi - i(\varphi - \theta_0)} - e^{\chi + i(\varphi - \theta_0)} \right] \\ &= \frac{2 (\sinh \psi \cos \varphi + i \cosh \psi \sin \varphi)}{e^{\psi} - \frac{a+b}{a-b} e^{-\psi}} \end{aligned}$$

the ellipse  $\psi_0$  we have from eq. 10-21

$$|\mathbf{H}| = \left| \frac{dW}{d\zeta} \right| = \frac{H^0 (a+b) \sin(\varphi - \theta_0)}{\sqrt{a^2 \sin^2 \varphi + b^2 \cos^2 \varphi}}$$

maximum of this expression is at the point where

$$\tan \varphi = -\frac{b^2}{a^2} \cot \theta_0, \quad \text{i. e., } \frac{y}{x} = -\frac{b^3}{a^3} \cot \theta_0$$

ameter of the ellipse is drawn in the direction  $\theta_0$ , the conjugate diameter to the tangents at the ends of the first one) is given by

$$\frac{y}{x} = -\frac{b^2}{a^2} \cot \theta_0$$

$\leq a$  the maximum field therefore lies considerably nearer to the axis of the ellipse than this diameter, except when  $\theta_0 = 0$  or  $\frac{1}{2}\pi$ . maximum value itself amounts to

$$|\mathbf{H}|_{\max} = H^0 \left( \frac{1}{a} + \frac{1}{b} \right) \sqrt{\frac{1}{a^2 \sin^2 \theta_0} + \frac{1}{b^2 \cos^2 \theta_0}} \quad (10-24)$$

For  $\theta_0 = 0$  the factor multiplying  $H^0$  becomes  $(1 + b/a)$  and is thus smaller than the factor 2 appearing in the circular cylinder. For  $\theta = \frac{1}{2}\pi$  however, the factor becomes  $1 + a/b > 2$ . This confirms the statement made in Chap. 1 (g) about the intensifying of the field. It is at once evident that this intensification is greater when the cylinder forces the field to diverge around its major axis than if it exposed only its minor axis to the field.

The expression 10-24 is needed to calculate the limiting value of  $H^0$  that destroys the superconductivity in the cylinder [Chap. 17 (f)].

## CHAPTER 11

### The Sphere in a Homogeneous Magnetic Field

(a) We introduce polar coordinates in space,  $r, \theta, \varphi$ , forming a right-handed system in that order (Fig. 11-1). The following equations hold for the curl of a vector  $\mathbf{A}$

$$\begin{aligned} \text{curl } \mathbf{A} &= \frac{1}{r \sin \theta} \left[ \frac{\partial}{\partial \theta} (\sin \theta A_\varphi) - \frac{\partial A_\theta}{\partial \varphi} \right] \\ \text{curl}_\theta \mathbf{A} &= \frac{1}{r \sin \theta} \frac{\partial A_r}{\partial \varphi} - \frac{1}{r} \frac{\partial (r A_\varphi)}{\partial r} \\ \text{curl}_\varphi \mathbf{A} &= \frac{1}{r} \frac{\partial (r A_\theta)}{\partial r} - \frac{1}{r} \frac{\partial A_r}{\partial \theta} \end{aligned} \quad (11-1)$$

The differential equation  $\Delta u - \beta^2 u = 0$  in these coordinates reads:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial u}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial u}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 u}{\partial \varphi^2} - \beta^2 u = 0 \quad (11-2)$$

We can solve this equation for the present problem by separation of the variables:

$$u = f(r) \sin \theta e^{i\varphi} \quad (11-3)$$

Direct calculation shows that

$$\frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial u}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 u}{\partial \varphi^2} = -\frac{2}{r^2} f(r) \sin \theta e^{i\varphi}$$

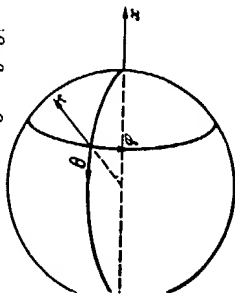
so we can divide eq. 11-2 by the factor  $\sin \theta e^{i\varphi}$  common to all terms and we are left with the ordinary differential equation for  $f(r)$ :

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{df}{dr} \right) - \left( \beta^2 + \frac{2}{r^2} \right) f = 0 \quad (11-4)$$

solution of this that remains finite at  $r = 0$  is

$$f(r) = \frac{1}{\beta r} \cosh(\beta r) - \left(\frac{1}{\beta r}\right)^2 \sinh(\beta r) \\ = \frac{(\beta r)}{3} + \frac{(\beta r)^3}{5 \cdot 3!} + \dots + \frac{(\beta r)^m}{(m+2)m!} + \dots \quad (11-5)$$

$f$  is positive because  $\tanh \beta r < \beta r$  for all positive values of  $r$ . For large values of  $\beta r$



$$f = \frac{1}{2} (\beta r)^{-1} e^{\beta r} \quad (11-6)$$

(b) Let the polar axis  $\theta = 0$  and likewise the positive  $x$  axis be in the direction of the homogeneous magnetic field. If the field were undisturbed its potential would be

$$\Phi = -H^0 r \cos \theta$$

1-1. The polar coordinates  $r, \theta, \varphi$ . The  $r$  arrow is pointed upwards.

If the sphere were completely impenetrable to the lines of force it would be a dipole, as shown by potential theory and as will be confirmed later. It would contribute to the potential a term of the form  $r^{-2} \cos \theta$ . Before in analogy to the procedure of Chap. 10 (c) we now seek a solution in the space outside the sphere in the form

$$\Phi = -H^0 \left( r + \frac{a}{r^2} \right) \cos \theta \quad (11-7)$$

$4\pi a H^0$  represents the magnetic moment of the sphere<sup>2</sup>. With  $a$  it is in the negative  $x$  direction and thus opposite to the field. magnetic field strength  $H = -\text{grad } \Phi$  follows immediately from 1-7:

$$H_r = -\frac{\partial \Phi}{\partial r} = H^0 \left( 1 - \frac{2a}{r^3} \right) \cos \theta \\ H_\theta = -\frac{1}{r} \frac{\partial \Phi}{\partial \theta} = -H^0 \left( 1 + \frac{a}{r^3} \right) \sin \theta \\ H_\varphi = 0 \quad (11-8)$$

can be expected from symmetry the lines of force lie in meridian planes  $\varphi = \text{constant}$ . According to Chap. 7 (c) the current must be perpendicular to the lines of force, at least for thick superconductors, and

together with  $r^{-1}$  itself, all its derivatives with respect to the rectangular coordinates  $x, y, z$  are also solutions of  $\Delta u = 0$ . But  $\partial(r^{-1})/\partial x = -x/r^3 = -\cos \theta/r^2$  we have chosen  $x = r \cos \theta$ . This is in Lorentz units. In electrostatic units the moment is  $a H^0$ .

near the surface, so we must expect it to flow along the latitude — circles  $r = \text{const}$ ,  $\theta = \text{constant}$ . Therefore for the interior of the sphere we try

$$i_r = i_\theta = 0, \quad i_\varphi = C(r) \sin \theta \quad (11-9)$$

If for  $f(r)$  we assume the same function as in eq. 11-5, then according to (a) the components of the current

$$i_r = -i_\theta \sin \varphi, \quad i_\varphi = i_\theta \cos \varphi$$

satisfy the differential equation  $\Delta u - \beta^2 u = 0$ . From the relation  $H = -c \lambda \text{curl } i$  we have from eq. 11-1:

$$H_r = -\frac{c \lambda}{r \sin \theta} \frac{\partial(\sin \theta i_\varphi)}{\partial \theta} = -\frac{2\sqrt{\lambda}}{\beta r} C(r) \cos \theta \\ H_\theta = -\frac{c \lambda}{r} \frac{\partial(r i_\varphi)}{\partial r} = \frac{\sqrt{\lambda} C}{\beta r} [\sinh(\beta r) - f(r)] \sin \theta \quad (11-10)$$

To check whether these equations are correct we show, as in Chap. 10 (c) that they fulfil the boundary conditions at the surface of the sphere  $r = R$ . These require the continuity of the two nonvanishing components of  $H$ . According to eqs. 11-8 and 11-10 we should have

$$H^0 \left( 1 - \frac{2a}{R^3} \right) = -\frac{2\sqrt{\lambda}}{\beta R} C(R) \\ H^0 \left( 1 + \frac{a}{R^3} \right) = \frac{\sqrt{\lambda} C}{\beta R} [f(R) - \sinh(\beta R)]$$

As a matter of fact we can satisfy these conditions by means of the adjustable constants  $a$  and  $C$ . For this purpose we have to put

$$C = -\frac{3H^0 \beta R}{2\sqrt{\lambda} \sinh(\beta R)}, \quad a = \frac{1}{2} \left[ 1 - \frac{3f(R)}{\sinh \beta R} \right] R^3 \quad (11-11)$$

Evidently  $i_\varphi$  is negative; the current flows against the arrow in Fig. 11-1. From eq. 11-10 we now have the equations

$$\frac{\partial}{\partial r} (r \sin \theta i_\varphi) dr + \frac{\partial}{\partial \theta} (r \sin \theta i_\varphi) d\theta = 0, \quad \text{i. e., } r \sin \theta i_\varphi = \text{constant}$$

or  $r f(r) \sin^2 \theta = \text{constant}$ . These, with  $\varphi = \text{constant}$ , determine the magnetic lines of force in the interior.

(c) The discussion proceeds in the same way as in Chap. 10 (c). From eqs. 11-9, 11-10, and 11-11 it follows that for a large sphere ( $\beta R \gg 1$ ) and high values of  $\beta r$  that

$$i_\varphi = -\frac{3H^0 R}{2\sqrt{\lambda} r} e^{-\beta(R-r)} \sin \theta \\ H_r = 0, \quad H_\theta = -\frac{3H^0 R}{2r} e^{-\beta(R-r)} \sin \theta \quad (11-12)$$

this means the formation of a protective layer around a field-free or. Furthermore, we conclude from eqs. 11-11 and 11-6 that

$$a = \frac{1}{2} \left( 1 - \frac{3}{\beta R} \right) R^3 \quad (11-13)$$

this value it follows from eq. 11-8 in agreement with eq. 11-12 that  $= R$ :

$$H_r = 0, \quad H_\theta = -\frac{3}{2} H^0 \sin \theta \quad (11-14)$$

ist equation proves that in this approximation the sphere appears the outside as if it were totally impenetrable to the lines of force; cond equation proves that the intensification of the field due to its tion leads to a maximum one and a half times the original field strength already mentioned in Chap. 1 (g). Figure 1-5 is valid qualitatively or the field distribution in a meridian plane of the sphere in spite fact that it is drawn for the cylindrical problem. For small  $\beta R$ , however, according to eq. 11-5  $f(R)$  becomes  $(1/3)\beta R$ , so eq. 11-11 we have

$$a = 0 \quad (11-15)$$

the same time  $C = -\frac{3H^0}{2\sqrt{\lambda}}$ , it follows from eq. 11-9 that

$$i_v = -\frac{1}{2} H^0 \left( \frac{\beta r}{\sqrt{\lambda}} \right) \sin \theta \quad (11-16)$$

om eq. 11-10 that

$$H_r = H^0 \cos \theta, \quad H_\theta = -H^0 \sin \theta \quad (11-17)$$

ling to the last equation  $\mathbf{H}$  is in the  $x$  direction and has the magnitude he magnetic field penetrates the sphere without hindrance as was expected from Chap. 7 (f), whereas eq. 11-16 for  $i_v$  has the same form as eq. 7-29. Choosing the length of the superconductor  $L$  to  $R$  in order to duplicate eq. 11-16 one has to put  $-\frac{1}{2}(\sqrt{\lambda}/R) \sin \theta$  pure number  $\tau_a$  which depends only on the position of the origin superconductor.

conclude from the expansion 11-5 and the known series

$$\sinh(\beta R) = \beta R + \frac{(\beta R)^3}{3!} + \frac{(\beta R)^5}{5!} + \dots + \frac{(\beta R)^{2m+1}}{(2m+1)!} \dots$$

$\sinh(\beta R)$  increases faster with increasing  $\beta R$  than  $f(R)$ . Therefore 11-11  $a$  grows monotonically with  $\beta R$  from 0 to  $\frac{1}{2}R^3$ , the magnetic

ollows from eq. 11-10 for the center of the sphere  $r = 0$  exactly

$$(\mathbf{H}_\theta)_{r=0} = \frac{H^0 \beta R \cos \theta}{\sinh(\beta R)}, \quad (\mathbf{H}_\theta)_{r=0} = -\frac{H^0 \beta R \sin \theta}{\sinh(\beta R)}$$

es  $\mathbf{H}$  the direction of the  $x$  axis, as was to be expected from symmetry, and nitude  $H^0 \beta R / \sinh(\beta R)$ . This can be used to confirm the mean value theorem -25.

moment  $4\pi a H^0$  goes from 0 to  $2\pi R^3 H^0$ , and the moment per unit volume and unit field strength increases from 0 to  $\frac{1}{2}$ .

A nonmagnetic layer, e. g., of colloidal spheres of mercury dispersed in gelatine, must become increasingly diamagnetic below the transition temperature, 4.17° K, the greater the moment per unit volume due to the spheres.

If there are  $N$  such spheres per unit volume, the latter has a moment  $4\pi a N H^0$ ; the permeability is therefore  $\chi = 4\pi a N$ . If each sphere has a radius  $R$  and they occupy a fraction  $V$  per unit volume, then  $N = 3V/4\pi R^3$  so that

$$\chi = \frac{3V}{\pi R^3} a$$

For large values of  $\beta R$ :

$$a = \frac{1}{2} R^3 \quad \text{according to}$$

eq. 11-13, and therefore the corresponding permeability

$$\chi_\infty = \frac{3V}{2\pi}$$

and in this way we get for  $\beta R \ll 1$  a somewhat better approximation than used above:

$$\frac{\chi}{\chi_\infty} = \frac{a}{\frac{1}{2} R^3} = 1 - \frac{3/(R)}{\sinh(\beta R)} = \frac{1}{15} (\beta R)^2 \quad (11-18)$$

(d) Shoenberg<sup>4</sup> [Chap. 1 (c)] used the above method to determine the superconductivity constant  $\lambda$  as a function of temperature. He knew from the amount of mercury in emulsion what the permeability  $\chi_0$  would be if the  $\beta R$  of the small spheres were great compared with unity. Actually the permeability was only some thousandths of this (see Fig. 11-2) and dropped much lower still as the transition temperature was approached. Shoenberg knew only that the average radius of the spheres was about  $0.5 \times 10^{-5}$  cm. To obtain information about  $\beta$  he started from eq. 11-18. If we indicate values of  $\chi$ ,  $\beta$ , and  $\lambda$  at  $T = 2.5^\circ \text{K}$  by an inferior 2.5, we have, from eqs. 11-18 and 6-7

$$\frac{\chi}{\chi_{2.5}} = \left( \frac{\beta}{\beta_{2.5}} \right)^2 = \frac{\lambda_{2.5}}{\lambda}$$

<sup>4</sup>D. Shoenberg, *Nature*, 143, 434 (1939).

E. Laumann and D. Shoenberg, *Nature*, 160, 747 (1948).

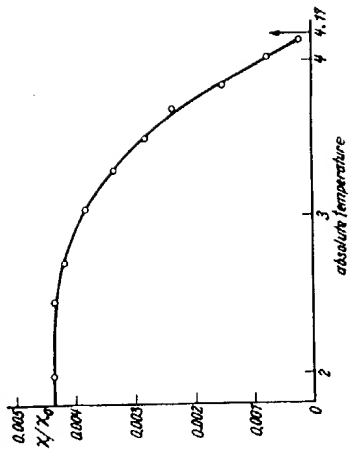


Fig. 11-2. Relative susceptibility of a slab containing superconducting colloidal mercury spheres as a function of temperature. (After Shoenberg.)



means of this equation Shoenberg was able to plot his experimental results as in Fig. 11-3, which shows  $1/\lambda/\lambda_{0,s}$  as a function of  $T$ . They agree well with the values found by Appleyard and co-workers<sup>3</sup> [Chap. 1 (c)] by another method [see Chap. 18 (e)].  $\lambda$  becomes infinite at  $T_s$  like  $(T_s - T)^{-1}$  because  $\lambda$  goes to zero like  $(T_s - T)$  in Fig. 11-2.

If we specify a line of force by its distance in the undistorted part of the field from the central line of force that is directed toward the center of the sphere, its equation can easily be derived from eq. 11-7 and reads

$$\left(r^2 - \frac{2a}{r}\right) \sin^2 \theta = C^2, \quad \varphi = \text{constant}$$

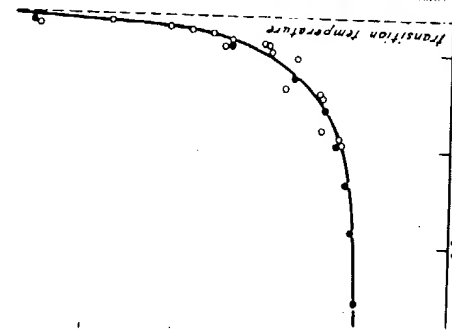


Fig. 11-3. The superconductivity constant  $\lambda$  varies as a function of temperature. ●, measurements of Appleyard, Bristow, and others; ○, measurements of Shoenberg.

The eqs. 11-9, 11-10, and 11-11 remain true for noncubic crystals. The ellipsoid of the tensor  $\lambda_{\alpha\beta}$  has rotational symmetry and the axis of symmetry lies in the  $z$  direction. Only then  $\beta$  can be replaced by  $z/\lambda_1$  where  $\lambda_1$  is the principal value of the tensor for a direction perpendicular to the axis of symmetry.

<sup>3</sup> Appleyard, T. R. Bristow, and H. London, *Nature*, **148**, 433 (1939).

## CHAPTER 12

### Persistent Currents

(a) A classical method for the treatment of electromagnetic problems uses the vector potential  $\mathbf{A}$  in conjunction with the scalar potential  $\phi$ . In the static case  $\phi$  becomes the electrostatic potential and it is therefore a generalization of the latter.  $\mathbf{A}$  and  $\phi$  are defined by requiring

$$\mathbf{B} = \text{curl } \mathbf{A} \quad (12-1)$$

$$\mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} - \text{grad } \phi \quad (12-2)$$

From these it follows at once that

$$\text{div } \mathbf{B} = 0, \quad \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = \frac{1}{c} \text{curl } \frac{\partial \mathbf{A}}{\partial t} = -\text{curl } \mathbf{E}$$

which agrees with the fundamental eqs. I and III (Chap. 3). To obtain the fundamental eqs. II and IV also, we must now add a condition on  $\text{div } \mathbf{A}$ , which we may do because no vector is completely defined by giving only its curl. We require that

$$\text{div } \mathbf{A} + \frac{\epsilon \mu}{c^2} \frac{\partial \phi}{\partial t} = 0 \quad (12-3)$$

According to eqs. 12-2 and 12-3 we now have

$$\text{div } \mathbf{D} = \text{div } (\epsilon \mathbf{E}) = \epsilon \text{div } \mathbf{E} + (\mathbf{E} \cdot \text{grad } \epsilon)$$

$$= -\frac{\epsilon}{c} \frac{\partial}{\partial t} \text{div } \mathbf{A} - \epsilon \Delta \phi + (\mathbf{E} \cdot \text{grad } \epsilon)$$

$$= \frac{\epsilon^2 \mu}{c^2} \frac{\partial^2 \phi}{\partial t^2} - \epsilon \Delta \phi + (\mathbf{E} \cdot \text{grad } \epsilon)$$

and if we subject  $\phi$  to the condition

$$\Delta \phi - \frac{\epsilon \mu}{c^2} \frac{\partial^2 \phi}{\partial t^2} = -\rho + \frac{1}{\epsilon} (\mathbf{E} \cdot \text{grad } \epsilon) \quad (12-4)$$

we recover eq. IV ( $\text{div } \mathbf{D} = \rho$ ). In order to obtain eq. II we use eqs. 12-1 and 12-3 and the vector rule 6-1 to obtain

$$\text{curl } \mathbf{B} = \text{curl } \text{curl } \mathbf{A} = \text{grad } \text{div } \mathbf{A} - \Delta \mathbf{A} = -\text{grad } \left( \frac{\epsilon \mu}{c^2} \frac{\partial \phi}{\partial t} \right) - \Delta \mathbf{A}$$

$$= -\frac{\epsilon \mu}{c} \left[ \frac{\partial \mathbf{E}}{\partial t} + \frac{1}{c} \frac{\partial^2 \mathbf{A}}{\partial t^2} \right] - \frac{1}{c} \frac{\partial \phi}{\partial t} \text{grad } (\epsilon \mu) - \Delta \mathbf{A} \quad (12-5a)$$

Also according to eqs. 3-2 and II:

$$\begin{aligned} \text{curl } \mathbf{B} &= \text{curl } (\mu \mathbf{H}) + \text{curl } \mathbf{M} = \mu \text{curl } \mathbf{H} - [\mathbf{H} \times \text{grad } \mu] + \text{curl } \mathbf{M} \\ &= \frac{\mu}{c} \left( \frac{\partial \mathbf{E}}{\partial t} + \mathbf{i} \right) - [\mathbf{H} \times \text{grad } \mu] + \text{curl } \mathbf{M} \end{aligned} \quad (12-5b)$$

necessary and sufficient condition for the validity of eq. 11 follows subtracting the right-hand sides of 12-5a and 12-5b:

$$\mathbf{A} - \frac{\epsilon \mu}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} = -\frac{\mu}{c} \mathbf{i} - \text{curl } \mathbf{M} + \frac{1}{c} \frac{\partial \phi}{\partial t} \text{grad}(\epsilon \mu) + [\mathbf{H} \times \text{grad} u] \quad (12-6)$$

accept eqs. 12-4 and 12-6 as valid throughout all space. The  $\mathbf{i}$  here means the sum of ohmic and supercurrents.

The most frequent application of eq. 12-1 consists in the transformation of the integral  $\int_C \mathbf{B} \cdot d\sigma$  over a surface  $C$  into the line integral and the boundary by Stokes' theorem:

$$\int_C (\mathbf{B} \cdot d\sigma) = \int_C (\mathbf{A} \cdot d\mathbf{s}) \quad (12-7)$$

Figure 12-1 shows the relation between the direction of the normal vector  $d\sigma$  and the sense  $d\mathbf{s}$  in which the line integral traverses the boundary. The justification for using the same symbol  $C$  to specify both surface and loop is that all surfaces with the same loop as boundary have the same integral  $\int_C (\mathbf{B} \cdot d\sigma)$  because of  $\text{div } \mathbf{B} = 0$ .

(b) We now have to explain the concept of the multiply connected region. In a simply connected or singly connected region of space two closed curves  $C$  and  $C'$  which lie completely within the region, but are otherwise quite arbitrary, can be transformed into each other by continuous deformation without either of them leaving the region. In particular  $C$  can be contracted to a point, because  $C'$  be chosen to be an infinitesimal loop around this point. Such curves exist in a doubly connected region; we call them curves of the first kind. Besides these there are curves of the second kind which can be transformed in the described manner into each other but not into curves of the first kind. It is impossible to reduce them to a point (Fig. 12-2a).

have to distinguish  $n$  sets of curves for an  $n$ -ply connected region. All curves of the same kind can be transformed into each other in the described manner but not curves of one set into curves of another set. possibility of reduction to a point is reserved for curves of the first kind. We assign once and for all the same arbitrary sense of traversal to curves of the same kind. The line integrals over such curves are defined along this sense of traversal, which we shall call the sense of the curve circuit.

Curves that can be reduced by continuous deformation to a curve  $C_1$  together a curve  $C_2$  within a triply connected region do not constitute a new kind of curve. Similar statement holds for  $n$ -ply connected regions.

In a singly connected region of space every finite and continuous scalar function  $\Psi$  is unique if its gradient is uniquely defined, e. g., by physical quantities, because for any closed curve  $C$  in the region

$$\int_C (d\mathbf{s} \cdot \text{grad } \Psi) = \int_C (d\sigma \cdot \text{curl grad } \Psi)$$

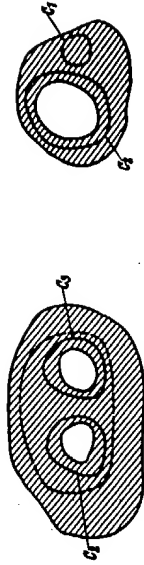


Fig. 12-2. (a) Curves  $C_1$  and  $C_2$  in a doubly connected region. (b) Curves  $C_1$  and  $C_2$  in a triply connected region. The dotted line is not a new kind of curve because it can be reduced to a curve  $C_1$  together with a curve  $C_2$ .

and the right side vanishes because  $\text{curl grad } \Psi \equiv 0$ . This conclusion holds only for curves of the first kind in a doubly connected region if  $\Psi$  is defined only within the region. Since these curves can be contracted to a point, we can draw surfaces of which they are the boundaries completely within the region of interest. For a curve of the second kind, such a surface necessarily extends outside the region. Otherwise it would also be possible to reduce these curves to a point. Consequently, for a curve of the second kind  $C_2$ ,

$$\int_{C_2} (d\mathbf{s} \cdot \text{grad } \Psi) = S_{C_2}$$

can differ from zero and be either positive or negative. However, the integral has the same value for all curves  $C_2$ . For two such curves  $C_2$  and  $C_2'$ ,

$$\int_{C_2'} (d\mathbf{s} \cdot \text{grad } \Psi) - \int_{C_2} (d\mathbf{s} \cdot \text{grad } \Psi) = \iint_{C_2' - C_2} (d\sigma \cdot \text{curl grad } \Psi)$$

The surface integral extends over a surface bounded by the curves  $C_2$  and  $C_2'$  lying completely within the region and is therefore zero because of the present theorem. In an  $n$ -ply connected region the integral  $\int (d\mathbf{s} \cdot \text{grad } \Psi)$  has the same value for all curves  $C_m$  (any given  $m \leq n$ ) but has different values for curves of different kind. It is zero for curves of the first kind, as before.

A doubly connected region is made simply connected by a cut  $Q$ , i. e., a surface intersecting every curve  $C_2$  once and only once, destroying all  $C_2$  as closed curves. All curves still remaining closed are now of the first kind. The boundaries of the cut necessarily lie in the surface of the region.

wise  $Q$  would not cut all the curves  $C_2$ . Except for this requirement is complete freedom of choice of position and form of  $Q$ . ( $n-1$ ) cross-sectional cuts  $Q_m$ , ( $m=2, 3, \dots, n$ ) are needed to produce a simply connected region from an  $n$ -ply connected one.  $Q_m$  cuts all closed curves  $C_m$  in the single region formed in this way only closed curves of the first kind exist and the scalar  $\Psi$  is unique in such a region. Consider two points 1 and 2 lying on opposite sides of, and immediately adjacent to, the cut  $Q_m$ . Ifers at 1 and 2 by

$$\Psi'_2 - \Psi'_1 = \int_1^2 (ds \cdot \text{grad } \Psi) = \int_{C_m} (ds \cdot \text{grad } \Psi) = S_{C_m} \quad (12-8)$$

oints 1 and 2 must be chosen in such a way that the path from 1 to 2 does not pass through the cut at  $Q_m$  has the same sense as the curve  $C_m$ .  $C_m$  has the same value for all curves  $C_m$  the jump in  $\Psi$  at the cut is the same for all points on it.

ese cuts are necessary if one wishes to apply Stokes' theorem in a simply connected region to a vector  $\Psi S$ , the product of a unique vector  $\Psi$ . Applied to the cut region

$$\begin{aligned} \int \text{div}(\Psi S) d\tau &= - \int \Psi S \cdot d\sigma \\ -(\Psi'_1 - \Psi'_2) \int_{C_m} (S \cdot d\sigma_1) &= S_{C_m} \int_{C_m} (S \cdot d\sigma_1) \end{aligned} \quad (12-9)$$

et that the two contributions do not in general cancel each other that the Gauss theorem can be applied directly only to singly connected regions. According to what has been agreed to about the points 2, the normal  $d\sigma_1$  has the same direction as the sense of the curves  $C_m$ . From eq. 12-1 and the fundamental equation X:  $H = -c \text{curl } G$  sows that

$$\text{curl}(cG + A) = 0 \quad (12-10)$$

ore a superconduction scalar potential  $\Psi$  exists for which

$$\text{grad } \Psi = cG + A \quad (12-11)$$

re is no supercurrent outside the superconductor this potential is only in the interior. The integral

$$\begin{aligned} S_C &= \int_C (ds \cdot \text{grad } \Psi) = \int_C ds (cG + A) \\ &= c \int_C G \cdot ds + \int_C A \cdot ds \end{aligned} \quad (12-12)$$

therefore has the value zero for any closed curve  $C$  in a singly connected superconductor; in a doubly connected superconductor (in the form of a ring) it is likewise zero for curves of the first kind, but has in general a unique value  $S_{C_2}$  different from zero. In an  $n$ -ply connected superconductor the integral has the same value  $S_{C_m}$  for all curves of the  $m^{\text{th}}$  kind. The superconduction potential  $\Psi$  is multiple valued ("periodic") with the "periods"  $S_{C_m}$ .

We differentiate eq. 12-10 with respect to time and use the fundamental equation IX ( $E = \partial G / \partial t$ ) and also eq. 12-2 to obtain

$$-c \text{grad } \phi = \text{grad } \frac{\partial \Psi}{\partial t} \quad (12-13)$$

The potential  $\phi$  is defined in all space, and is therefore unique. Integrating eq. 12-12 over a closed curve  $C_m$  within the superconductor:

$$\frac{d}{dt} \int_{C_m} (ds \cdot \text{grad } \Psi) = \frac{dS_{C_m}}{dt} = 0 \quad (12-14)$$

The integrals  $S_C$  do not change with time so long as the specimen remains superconducting. This is still true if during a phase transition the superconducting material grows at the expense of the normal material so causing the ring to become thicker, or, if it shrinks, by the reverse process.

The explanation of the persistent current contained in these theorems is due to F. London. All experiments on the persistent current have been done with doubly connected superconductors, e. g., in the form of a ring or a closed coil. Moreover, the superconductor has always been thick compared with the penetration depth. If the curve  $C_2$  be placed in the field-free interior,  $G = 0$  on the curve and it follows from eq. 12-11 that

$$S_C = \int_C B \cdot d\sigma \quad (12-15)$$

From this eq. 12-13 shows that the flux of induction through any surface  $\sigma$  that encloses the bore of the ring and protrudes through the protective layer into the field free interior (which adds but little) is constant, see Fig. 12-3.

Therefore if a ring has been placed in a magnetic field while still above its transition temperature, and if on cooling below the transition a certain flux of induction is trapped in the bore of the ring, this will remain there until superconductivity is destroyed: it is "frozen in." If the external field

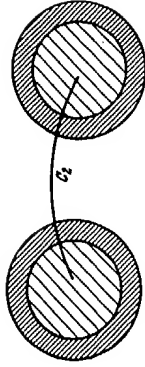


Fig. 12-3. Illustrating a curve  $C_2$  lying entirely within the field-free bore of a ring. Darkly shaded area represents the protective layer; lightly shaded area represents the protected interior.

witched off, the ring acts as a permanent magnet due to this flux of induction. The great achievement of the London theory is that it logically combines this freezing-in process with the Meissner effect, i. e., the fact that the field inside a superconductor does not get frozen in but is expelled. If a superconducting ring initially free of current is placed in a magnetic field, the lines of force will go around it according to eq. 12-14; its bore acquires a permanent field free.

It should be emphasized once more that eq. 12-14 holds only for "thick" rings; for "thin" ones the line integral in  $S_C$  (eq. 12-11) cannot be neglected. Such rings the flux of induction does not freeze in. Immediately below transition temperature every specimen is effectively thin, as has been repeatedly pointed out. The flux which according to eq. 12-14 remains constant, is not necessarily identical with the flux that passed through the bore before the ring became superconducting.

The ohmic current has not been mentioned in the above discussion. It does not mean that it is zero under the circumstances of the problem, but that we have neglected it. On the contrary our conclusions are completely rigorous and independent of what happens to the ohmic current when the changes under consideration. Strictly speaking, the ohmic current has always to play its role as consumer of energy during the process, the more strongly the more rapid the process. The fact that the rate of change of this kind can be detected in actual experiments, is due to the very slow rate of change at practicable frequencies.<sup>2</sup>

In multiply connected specimens carrying a persistent current the superconductor is certainly not zero everywhere, according to the argument in the text. If we may ask whether perhaps it does not vanish identically for a singly connected superconductor in a static magnetic field? This question has to be answered negatively, in so far as we understand by  $A$  the potential introduced in (4) and (5) the total magnetic field. This can already be seen for the cubic crystal especially simple conditions prevail because  $\mathbf{H}$  and  $\mathbf{G}$  have the same directions. To eq. 12-10 and the boundary condition  $\mathbf{H}_t = 0$  (and therefore also  $\mathbf{G}_n = 0$ ) it must be added

$$\frac{\partial \Psi}{\partial n} = A_n$$

is certainly not generally true that  $A_n = 0$ . However, by relinquishing the condition of the whole field, we could introduce a potential for the interior of the superconductor alone:

$$\mathbf{A}' = \mathbf{A} - \text{grad } \Psi$$

the potential we should have

$$\text{curl } \mathbf{A}' = 0$$

in 12-1 would be retained in the form  $\mathbf{H} = \text{curl } \mathbf{A}'$ . Whereas according to 3  $\text{div } \mathbf{A} = 0$  for stationary fields generally, the relation  $\text{div } \mathbf{A}' = 0$  would follow from eq. 12-10 only for cubic crystals. It is only for these crystals that the condition  $\text{div } \mathbf{G} = 0$  follows from  $\text{div } \mathbf{H} = 0$ . Because of this restriction, no special condition can be attached to the potential  $\mathbf{A}'$ .

(d) Let us calculate the "period" of the superconduction potential

$$S_C = \int \mathbf{H} \cdot d\sigma = 2\pi \int_0^R r H_t dr$$

in the example of a hollow cylinder of cubic crystal material, with an inner radius  $R$  and field  $H_t$  in the interior hollow space [Chap. 9 (a)]. The integral with respect to  $r$  should extend as far as a circle situated in the protected field-free space inside the superconductor. This is expressed in the formula by writing the upper limit as infinite.

Now for  $r < R$ ,  $H_t = H_i$ , whereas for  $r > R$ , according to eq. 10-7

$$H_t = H_i \frac{H_0(i\beta R)}{H_0(i\beta r)}$$

so according to the theorem

$$\int_0^\infty H_0(z) dz = -x H_1(x)$$

we obtain

$$S_C = 2\pi R^2 H_i \left[ \frac{1}{2} - \frac{1}{i\beta R} \frac{H_1(i\beta R)}{H_0(i\beta R)} \right]$$

The second term in the bracket is positive real, as it should be, because both  $iH_0(i\beta R)$  and  $-H_1(i\beta R)$  are also positive real. For large  $\beta R$  this term is vanishingly small compared with the first term because the ratio of the two Hankel functions becomes unity. For small  $\beta R$ , however, it becomes the dominant term, even increasing without limit as  $\beta R$  decreases, because  $-H_1(i\beta R)$  becomes  $2/\pi \beta R$ , and  $iH_0(i\beta R) \rightarrow -(2/\pi) \ln(\beta R)$  in this limit. Thus we get

$$S_C = -\frac{2\pi H_i}{\beta^2 \ln(\beta R)} \quad (12-15)$$

$S_C$  therefore vanishes when  $R = 0$  as in this case, of course, the hollow cylinder becomes a simply connected solid cylinder.

If we imagine the temperature of a given hollow cylinder to be increased, then its  $\lambda$  increases, and consequently  $\beta$  and  $\beta R$  decrease, approaching zero when the transition temperature  $T_c$  is reached. The factor multiplying  $H_i$  increases without limit, and since  $S_C$  remains constant, according to what has been said above,  $H_i$  must accordingly decrease. The physical reason for this is the increase in the penetration depth  $\beta^{-1}$ . The field penetrates the superconductor and spreads over a continuously increasing area, so its intensity has to decrease because of the constancy of the total flux  $S_C$ . The superconduction potential  $\Psi$  is proportional to the angle  $\theta$  because of axial symmetry: thus

$$\Psi = \frac{\theta}{2\pi} S_C$$

and  $\Psi$  satisfies the potential equation<sup>3</sup>  $\Delta \Psi = 0$ . This must be so for all stationary currents in cubic-crystal superconductors according to eqs. 12-10 and 12-3 because from  $\text{div } \mathbf{i} = 0$  it follows for such crystals that  $\text{div } \mathbf{G} = 0$ . (c) When there is a persistent current in a ring, it has a magnetic moment. Does the direction of the moment depend on the way in which it is been produced? This and similar questions are answered by the uniqueness theorem for a superconductor in a stationary field. We derive now under the assumption that no ohmic current is supplied from outside. We form the scalar product of 12-10 with  $\mathbf{i}/2c$ , and integrate over volume of an arbitrary (homogeneous or inhomogeneous) superconductor indicated by the suffix  $s$  under the integral sign. This yields

$$\frac{1}{2} \int_s (\mathbf{i} \cdot \mathbf{G}) d\tau + \frac{1}{2c} \int_s (\mathbf{A} \cdot \mathbf{i}) d\tau = \frac{1}{2c} \int_s (\mathbf{i} \cdot \text{grad } \Psi) d\tau \quad (12-16)$$

using the formula

$$(\mathbf{i} \cdot \text{grad } \Psi) + \Psi \text{div } \mathbf{i} = \text{div } (\Psi \mathbf{i})$$

right-hand integral in eq. 12-16 can be transformed into

$$-\frac{1}{2c} \int_s (\Psi \text{div } \mathbf{i}) d\tau - \frac{1}{2c} \int_s \Psi (\mathbf{i} \cdot d\sigma)$$

because of the assumed stationary conditions in the interior, the fundamental eq. VI becomes  $\text{div } \mathbf{i} = 0$ , and at the surface eq. 3-7 gives 0. Therefore nothing remains of the above expressions except the contribution of the cross-sectional cuts which eventually have to be induced. For the time being we assume the superconductor to be doubly rected so we need only one cut. By eq. 12-8 its contribution is

$$-\frac{1}{2c} (\Psi_1 - \Psi_2) \int_{\sigma} \mathbf{i} \cdot d\sigma_1 = \frac{1}{2c} S_c \int_{\sigma} \mathbf{i} \cdot d\sigma_1 \quad (12-17)$$

write

$$\int_{\sigma} \mathbf{i} \cdot d\sigma_1 = I_s \quad (12-18)$$

current in the ring. As  $d\sigma_1$  is in the same direction as the curves  $C_2$ , positive if the current flows in the same sense as  $C_2$ , otherwise it is negative. Equation 12-16 is transformed in this way into

$$\frac{1}{2} \int_s (\mathbf{i} \cdot \mathbf{G}) d\tau = \frac{S_c I_s}{2c} - \frac{1}{2c} \int_s (\mathbf{A} \cdot \mathbf{i}) d\tau \quad (12-19)$$

On the other hand, the magnetic energy of the field is, by eqs. 5-8 and 3-2

$$\frac{1}{2} \int_s \mu H^2 d\tau = \frac{1}{2} \int_s (\mathbf{H} \cdot \mathbf{B}) d\tau = \frac{1}{2} \int_s (\mathbf{H} \cdot \mathbf{M}) d\tau$$

is the imaginary part of the complex function  $\ln(x + iy)$ .

where the suffix  $V$  indicates that the integral extends over the whole of space, whereas the suffix  $P$  indicates that it extends over only the permanent magnets in the field. By eq. 12-1 and the rule 5-1 we have

$$\frac{1}{2} \int_V (\mathbf{H} \cdot \mathbf{B}) d\tau = \frac{1}{2} \int_V (\mathbf{H} \cdot \text{curl } \mathbf{A}) d\tau = \frac{1}{2} \int_V (\mathbf{A} \cdot \text{curl } \mathbf{H}) d\tau - \frac{1}{2} \int_P ([\mathbf{A} \times \mathbf{H}] \cdot d\sigma)$$

The surface integral vanishes over the sphere at infinity because there  $\mathbf{H}$  behaves like  $R^{-3}$ . The tangential components of  $\mathbf{H}$  and  $\mathbf{A}$  are continuous at surfaces of discontinuity, therefore the normal component of  $[\mathbf{A} \times \mathbf{H}]$  which depends only on these tangential components is also continuous and does not contribute anything. Therefore

$$\frac{1}{2} \int_V \mu H^2 d\tau = \left( \frac{1}{2c} \right) \int_V (\mathbf{A} \cdot \mathbf{i}) d\tau - \frac{1}{2} \int_P (\mathbf{H} \cdot \mathbf{M}) d\tau \quad (12-20)$$

The field is produced by the ohmic current in the normally conducting coils together with the corresponding supercurrent in the superconductor, and also by any persistent current that may be present. We designate the coils by the suffix  $c$  under the integral sign. Splitting up the right-hand side of eq. 12-20 in this way yields:

$$\frac{1}{2} \int_V \mu H^2 d\tau = \frac{1}{2c} \int_s (\mathbf{A} \cdot \mathbf{i}) d\tau + \frac{1}{2c} \int_c (\mathbf{A} \cdot \mathbf{i}) d\tau - \frac{1}{2} \int_P (\mathbf{H} \cdot \mathbf{M}) d\tau$$

Adding this equation to 12-19 we get

$$\frac{1}{2} \int_s (\mathbf{i} \cdot \mathbf{G}) d\tau + \frac{1}{2} \int_V \mu H^2 d\tau = \frac{1}{2c} \left\{ S_c I_s + \int_c (\mathbf{A} \cdot \mathbf{i}) d\tau \right\} - \frac{1}{2} \int_P (\mathbf{H} \cdot \mathbf{M}) d\tau \quad (12-21)$$

According to eq. 5-8 the left-hand side of this is the total energy of the field  $U$ , which is necessarily positive or zero, the latter only if  $\mathbf{i} = 0$  and  $\mathbf{H} = 0$  everywhere. This equation implies the following theorem.

The "period"  $S_c$  of the superconduction potential in the ring, together with the ohmic currents and the permanent magnets determine uniquely the magnetic field of the supercurrent. This is because if we assume two different fields with the same ohmic currents and permanent magnets, the difference between the two fields also satisfies the differential equations of the London theory. Therefore eq. 12-21 may be expressed in terms of this difference, but the right-hand side vanishes by hypothesis.

For a singly connected superconductor the first term of the right-hand side is missing; it is therefore current free in the absence of external excitation; otherwise the apparatus producing the field determines the situation uniquely. This theorem also guarantees the uniqueness of the solution of those examples in Chaps. 10 and 11 which are not covered already by the uniqueness theorem of eq. 7-4. Equation 12-21 admits the possibility of an independent persistent current in a ring, but otherwise the ring is determined in all details by specifying its  $S_c$ . For instance its

magnetic moment is equal to  $ScP$  where  $P$  is a vectorial factor depending on the geometry of the ring and the intensive functions of position  $\lambda, \rho, Sc$  decides which one. In so far as the persistent current alone is exciting field, the direction of the current is such as to make  $ScI$  positive. as in Fig. 12-1 the current flows in the positive sense, assigned to all  $C_2$  in the ring, then the magnetic lines of force that pass through the ring have the direction of  $d\vec{a}$ , i. e., they come toward the reader. we place a ring carrying a persistent current in an additional external magnetic field, then an induced current is superposed on the original current, spite of the constancy of  $Sc$  the resulting current strength it can become zero or even reverse in sign.

Let a normally conducting specimen be placed in a magnetic field and cooled down until it becomes superconducting; then there is a considerable flux of induction through the ring but no current, or only very weak current. Which of these possibilities is realized depends upon detailed course of events during the cooling process and is difficult to determine. Switching off the magnetic field does not change the flux, the current increases to the strength determined by the total flux and form of the specimen. This is a common method of producing persistent currents.

To generalize eq. 12-21 for an  $n$ -ply connected superconductor we place the one term  $ScI$  by  $(n-1)$  terms of the same kind. The corresponding statement applies if several separate superconductors are present in the field.

Because of its magnetic moment every superconductor that has a persistent current must experience a torque in a homogeneous magnetic field in addition to that due to field deformation caused by the shape of specimen.<sup>4</sup>

(f) Let us assume two superconductors, both with persistent currents and  $I'$ , to be moving relative to each other. The forces between them perform work, and for lack of any other source of energy, at the expense of the energy  $ScI + Sc'I'$ . Because  $Sc$  and  $Sc'$  are constants according to eq. 12-14 a change of energy is only possible by a change of the strengths of the currents.

Suppose the superconductors to be rings formed by circles rotated around a common axis of symmetry that do not intersect the circles (Fig. 12-4). Let them be in such a relative position that at first they are at a great distance from each other and their axes of symmetry coincide. In this situation let the

Why is it that there is in the theory of ohmic currents and their magnetic fields, uniqueness theorem corresponding to eq. 12-21? This is because in this case the distribution of current density is answered uniquely by electrostatics and because solving this problem the magnetic field can be deduced unambiguously from current density. It is impossible to separate the problem of the superconductor into two parts in this way.

current  $I$  flow in the first ring, but zero current in the second one. Let the rings now be brought together. The resulting lines of force are then as sketched diagrammatically in the figure. If the current  $I$  flows away from the reader on the right-hand side (at the minus sign), then the current in the second ring flows toward the reader on the right-hand side. This follows from the rule [Chap. 7 (c)] that inner normal of the conductor, current, and magnetic field form a right-handed system. The antiparallel currents  $I_1$  and  $I_2$  repel each other; bringing the rings together requires the performance of work and produces an increase of the field energy  $ScI_1 I_2$  and thus an increase of  $I_2$ . However  $I_2'$  is also increased because the lines of force crowd together near the second ring and create a greater field strength the smaller the distance.

If a current  $I_2^0$  is initially flowing in the second ring when at infinite separation, then the current  $I_2^0 - I_2$  flows at the smaller distance, and there is attraction or repulsion depending on whether this expression is positive or negative. We have a stable equilibrium, at least with respect to motion along the axis, because a further approach leads to repulsion, and increase of distance to attraction. For example, in Justi's persistent current electro-magnet the current strength decreases when it is attracting iron and the flux of induction remains constant [Chap. 1 (b)].

(g) A famous experiment performed in 1924 is in apparent contradiction to this argument. Kamerlingh-Onnes<sup>5</sup> excited a persistent current in a hollow sphere of lead and so apparently in a singly connected region. He produced the current by the usual method of bringing the specimen, while at a higher temperature, into a magnetic field and then cooling it to become superconducting. The sphere showed a magnetic moment after removing the field and experienced the corresponding torque in any external field. This great investigator concluded that the paths of the current could not be displaced in the superconducting body. If they could be, the forces exerted by the external field would be unable to move the sphere because it has no preferential direction.

From later experience the following explanation can be given for the above observation. The cooling of the hollow sphere immersed in liquid helium did not proceed everywhere with the same speed. At first one or may be several annular zones became superconducting while the rest of

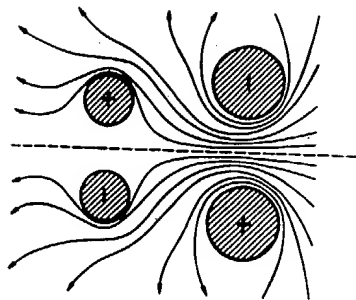
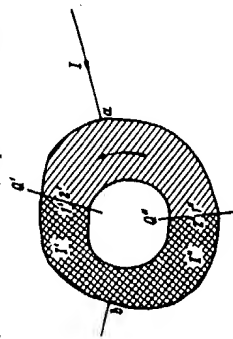


Fig. 12-4. Two superconducting rings with magnetic field lines.

<sup>5</sup>H. Kamerlingh-Onnes, *Commun. Leiden Supplement*, 50a, (1924).

sphere remained normal. With the approach of temperature equilibrium whole sphere had not become superconducting; instead, after the first had once trapped a certain amount of flux, the latter remained hanging in the nonsuperconducting remainder of the sphere which had in the intermediate state (Chap. 19). With increasing concentration the lines of force as the annular ring of superconducting material grew the cross section of the normal material decreased, the field strength eased finally beyond the critical value  $H_c$  in the rest of the sphere and prevented the complete establishment of the superconducting state.

Actually therefore the supercurrent was flowing in one or in several rings. Its magnetic moment was attached rigidly to this ring, and therefore also to the sphere, so the latter was forced to orient itself in an external field. This follows inevitably from the uniqueness theorem. However, even though Kamerlingh-Onnes failed to interpret his experiments, his question whether the current lines are displaced in a superconductor under the influence of an external magnetic field is still perfectly legitimate. This is discussed in Chap. 13.



12-5. Superconducting ring with normal conducting leads. The arrow shows 'sense' of the ring and also the positive current direction. A positive current  $I''$  in the opposite direction. The sense of ring is from 2' to 1' and from 2'' to 1''.

$h)$  In the examples discussed in the last paragraph and in section (d) is assumed that no ohmic current was supplied to the doubly connected reactor from outside. But now let us imagine that at two points  $a$  and  $b$  on the surface of the superconductor, normally conducting wires ordered through which a current  $I$  is supplied, entering at  $a$  and leaving see Fig. 12-5. The ohmic current is distributed through the superconductor with a current  $I'$  flowing in the path that goes from  $a$  to  $b$  in same direction as the "sense" of the ring (which we arbitrarily choose for all from "2" to "1"), and a current  $I''$  in the other path. We regard currents as positive if they are flowing from  $a$  to  $b$ . However, we from Chap. 2 that one of them can be negative. This is true particularly persistent current is superimposed on the supplied current. In general  $I' + I'' = I$  (12-22)

modified assumption does not alter eq. 12-10. Therefore eqs. 12-11 12-13 together with the theorems derived from them remain valid. the integral on the right-hand side of eq. 12-16

$$\int (\mathbf{i} \cdot \text{grad } \Psi) d\tau = - \int \Psi (\mathbf{i} \cdot d\sigma)$$

acquires another value because it is no longer true that  $\mathbf{i} \cdot \mathbf{e} = 0$  everywhere over the surface. Suppose the cut that contributes to the integral is made first in the branch carrying the current  $I'$ ; this cut may be called  $Q'$  and the function  $\Psi$  for this case will be written  $\Psi'$ . The integral then becomes

$$-(\Psi'_a - \Psi'_b)I + S_C I'$$

If we displace the cut to the other branch and call it  $Q''$ , and the corresponding function  $\Psi''$ , the surface integral becomes in the same way

$$-(\Psi''_a - \Psi''_b)I - S_C I''$$

Here  $I''$  has a minus sign because a positive  $I''$  has, by hypothesis, a direction opposite to the sense of the ring. The two values are equal because their difference

$$[(\Psi'_a - \Psi'_b) - (\Psi''_a - \Psi''_b)]I - (I' + I'')S_C = 0$$

This can be seen in the simplest way from eq. 12-22 by making use of the undetermined additive constant in the definition of  $\Psi'$  to make  $\Psi'_a = \Psi''_a$ . In this case  $\Psi'$  and  $\Psi''$  are equal throughout the whole singly shaded region in Fig. 12-5 between the two cuts that enclose the point  $a$  whereas in the other cross-hatched area between the two cuts enclosing the point  $b$  we have  $\Psi'' - \Psi' = S_C$ . Equation 12-21 is now replaced either by

$$\frac{1}{2} \int (\mathbf{i} \cdot \mathbf{G}) d\tau + \frac{1}{2} \int \mu \mathbf{H}^2 d\tau = \frac{1}{2c} [(\Psi'_b - \Psi'_a)I + S_C I' + \int (\mathbf{A} \cdot \mathbf{i}') d\tau] - \frac{1}{2} \int (\mathbf{H} \cdot \mathbf{M}) d\tau \quad (12-23)$$

or by

$$\frac{1}{2} \int (\mathbf{i} \cdot \mathbf{G}) d\tau + \frac{1}{2} \int \mu \mathbf{H}^2 d\tau = \frac{1}{2c} [(\Psi''_b - \Psi''_a)I - S_C I'' + \int (\mathbf{A} \cdot \mathbf{i}'') d\tau] - \frac{1}{2} \int (\mathbf{H} \cdot \mathbf{M}) d\tau$$

the term containing  $S_C$  has the positive or negative sign if the current is in the positive sense  $I'$  or the negative sense  $I''$  respectively. This agrees with the sign of the corresponding term in eq. 12-21.

This alteration does not affect the uniqueness theorem which we linked with eq. 12-21 because the current  $I$  supplied to the superconductor belongs to the ohmic currents of the external field. Also  $I$  becomes zero for the difference field between two fields corresponding to the same "period".  $S_C$  the same ohmic currents, and the same permanent magnets.

(i) Considered as the source of its field, a persistent current has, according to eq. 12-21, only the energy  $U = S_C I^2$ . However,  $S_C$  is proportional to  $I^2$ , and we may write

$$\frac{S_C}{c} = \frac{p^2}{c} \quad (12-24)$$

and we see from the equation

$$U = \frac{1}{2} \dot{p}^{ss} I_s^2 \quad (12-25)$$

that  $\dot{p}^{ss}$  is the coefficient of self-induction of the superconducting ring. It differs from the self-induction for an ohmic current in that in  $U$  there is also in  $\dot{p}^{ss}$  a positive term due to the energy of the supercurrent. However, this term is usually quite insignificant compared with the magnetic energy, because the superconductivity occurs for the most part only in thin layers where, due to the continuity of the components  $H$ , most of the energy density is of the same order of magnitude as in the joining parts of the outside space (see eq. 7-37). This positive contribution is annulled in thick specimens by the far greater negative contribution from the expulsion of the field.<sup>6</sup> This idea can be carried through quantitatively for special cases because the external magnetic field outside a superconductor is generally different from that for an ohmic conductor.

From eqs. 12-14 and 12-24 it follows that for a thick superconductor the coefficient of self-induction is equal to the flux through its own current circuit divided by the velocity of light  $c$  and the current strength. For superconductors there is a correction according to eq. 12-11. It is well known that this theorem does not hold for normal conductors, because it is then impossible to define the flux through its own current circuit in so far as the latter is considered to have extension in space, whereas it is considered infinitely thin, the flux is no longer finite. If there are ohmic currents of strength  $I^e$  present in addition to the supercurrent, we get

$$S_C = \dot{p}^{ss} I_s + \sum_e \dot{p}^{ee} I^e$$

linear function of all the current strengths. Furthermore, because the vector potential  $A$  is a linear sum of all the contributions from the separate currents, eq. 12-21 gives for the field energy, omitting the magnetic contribution,

$$U = \frac{1}{2} \sum_s \dot{p}^{ss} I_s I_s$$

the summation is extended over all the ohmic currents as well as the supercurrent. The coefficients of induction between the persistent current and the ohmic currents are also affected by the energy of the supercurrent in the same way as the self-induction  $\dot{p}^{ss}$ . Beyond this we say nothing without further information about the effect of the induction of the field.

<sup>6</sup>However, in a cable with the return path formed by its shell at a small distance from the inner conductor, supposing the shell to be superconducting, the superconductivity energy could be responsible for almost one-half of the coefficient of induction.

With regard to the other coefficients, the self-induction and the mutual inductions between the ohmic currents are also affected by the presence of the superconductor, just as they depend on the magnetic permeability in their neighborhood. One method for measuring the penetration depth  $\beta^{-1}$  and the constant  $\lambda$  is based on this fact. It was devised by Casimir<sup>7</sup> and used with success by Laurmann and Shoenberg<sup>8</sup>, although not absolute, it gives the dependence on temperature. A long solenoid is wound around a superconducting cylinder and a shorter induction coil is wound tightly around its center; their mutual induction is measured. The greater the penetration depth, the greater the flux of induction through the measuring coil due to the long solenoid, and so the greater their mutual induction. Two different specimens of mercury gave slightly different results in this experiment, and this is a reminder of the fact that the constant  $\lambda$  is really a tensor.

## CHAPTER 13

## The Maxwell and London Stresses

(a) Kamerlingh-Onnes in 1924 raised the question whether the track of the supercurrent could be displaced in the superconductor under the influence of an external magnetic field (see Chap. 12 (g)). He started from the assumption that in any case in the steady state the carriers of the supercurrent do not experience any forces due to the material itself, i. e., to the atoms and the carriers of the ohmic current, for otherwise persistent currents would be impossible. His question was, however, inconsequential in so far as the supercurrent already has its own magnetic field, so that the problem exists even before any external field enters the picture. Our present ideas about the current distribution had not been developed in 1924. We now have a clear picture of the current concentration in the protecting layer and we know that the current, magnetic field, and the inner normal to the surface form a right-handed system (Chap. 7), and therefore that the force per unit volume  $\frac{1}{2} [i \times H]$  due to its own magnetic field is directed toward the interior of the superconductor (current, field, and force also form a right-handed system). We may therefore raise the question: Why does the magnetic field not push the current into the interior? How can the current in the thin protecting layer have any stability at all?

Another question is intimately connected with this. A rod carrying a supercurrent  $I$  and located in a magnetic field  $H$  perpendicular to the axis of the cylinder, experiences a force  $\frac{1}{2} I H$  per unit length. Upon what does this force act? If the supercurrent mechanism experiences no force

<sup>7</sup>H. G. B. Casimir, *Physica*, 7, 887 (1940).

<sup>8</sup>E. Laurmann and D. Shoenberg, *Nature*, 160, 747 (1948).



to the material, neither can it exert force on the material: action and reaction must be equal. And yet the force due to the magnetic field certainly has to act first on the supercurrent mechanism, and through this somehow on the rod.

The answer can only be that the forces act on the material discontinuity the surface. It is there that the interaction between matter and the percurrent carriers must be located, and not in the interior. If such forces are not present even at the surface, the carriers would be able to escape from the metal, which certainly does not happen. The theory answers these questions in terms of the London stresses. The force ordinarily exerted by the field can be calculated from the divergence of the Maxwell stresses, which are defined in terms of the electric and magnetic fields; similarly the London stresses, which depend only on the supercurrent, are the divergence of the force exerted by the magnetic field on the supercurrent mechanism, and in fact locate it at the surface instead of throughout the body of the material. The supercurrent hangs as it were from the surface of a curtain, the magnetic field of the current corresponds to the weight of the curtain, the London stresses correspond to the elastic forces holding the curtain to its curtain rod and prevent it from falling into the interior. This is how we can answer Kamenlitch-Onnes' question.

The point therefore is to find a stress tensor that depends only on the current density  $\mathbf{i}$  and that has a divergence that everywhere just compensates the force resulting from the Maxwell stresses in the magnetic field.<sup>1</sup> London's fundamental equations IX and X are needed to carry this through mathematically. They enter as the necessary and sufficient conditions for the system of London stresses to just compensate the Maxwell stresses. The whole current distribution is fixed by this equilibrium condition: regard the fact that it makes such a compensation possible as inherently the strongest point in favor of the theory.

This compensation is not entirely necessary for inhomogeneous superconductors or non stationary currents. The discussion of the generalization 13-10 actually leads to completely new points of view.

(b) To begin with we define nine quantities in terms of two arbitrary vector functions of position  $\mathbf{P}$  and  $\mathbf{Q}$ :

$$\Theta_{\alpha\beta}(\mathbf{P}, \mathbf{Q}) = \mathbf{P}_\alpha \mathbf{Q}_\beta - \frac{1}{2} \delta_{\alpha\beta} \Sigma_\gamma \mathbf{P}_\gamma \mathbf{Q}_\gamma \quad (\alpha, \beta = 1, 2, 3) \quad (13-1)$$

they form the components of a tensor of the second rank because the two  $\mathbf{P}_\alpha \mathbf{Q}_\beta$  and  $\frac{1}{2} \delta_{\alpha\beta} \Sigma_\gamma \mathbf{P}_\gamma \mathbf{Q}_\gamma$  are each tensors themselves.<sup>2</sup> Written in a more detail the definition 13-1 reads:

$$\Theta_{11}(\mathbf{P}, \mathbf{Q}) = \frac{1}{2} (\mathbf{P}_1 \mathbf{Q}_1 - \mathbf{P}_2 \mathbf{Q}_2 - \mathbf{P}_3 \mathbf{Q}_3) \\ \Theta_{23} = \mathbf{P}_2 \mathbf{Q}_3, \quad \Theta_{32} = \mathbf{P}_3 \mathbf{Q}_2, \quad \text{etc.} \quad (13-2)$$

<sup>1</sup>As we later put  $-\text{div } \Theta$  equal to the force acting on the material we have to add a positive  $\Theta_{\alpha\alpha}$  as a pressure, a negative one as a tension.  
<sup>2</sup> $\delta_{\alpha\beta} = 1$  for  $\alpha = \beta$ , otherwise zero.

We now form the divergence of this tensor, i. e., the vector of which the  $x_1$  component is<sup>3</sup>

$$\text{div}_1 \Theta(\mathbf{P}, \mathbf{Q}) = \frac{\partial \Theta_{11}}{\partial x_1} + \frac{\partial \Theta_{12}}{\partial x_2} + \frac{\partial \Theta_{13}}{\partial x_3} \quad (13-3)$$

Carrying through the calculation yields

$$\text{div}_1 \Theta(\mathbf{P}, \mathbf{Q}) = \mathbf{Q}_1 \text{div } \mathbf{P} - [\mathbf{P} \times \text{curl } \mathbf{Q}]_1 + \frac{1}{2} \left( \sum_\gamma \mathbf{P}_\gamma \frac{\partial \mathbf{Q}_\gamma}{\partial x_1} - \sum_\gamma \mathbf{Q}_\gamma \frac{\partial \mathbf{P}_\gamma}{\partial x_1} \right) \quad (13-4)$$

Now we set  $\mathbf{P} = \mathbf{i}$ ,  $\mathbf{Q} = \mathbf{G}$ , i. e.,  $\mathbf{Q}_\alpha = \sum_\beta \lambda_{\alpha\beta} \mathbf{i}_\beta$  (see eq. VIII Chap. 3); then because of the symmetry relation 3-3 ( $\lambda_{\alpha\beta} = \lambda_{\beta\alpha}$ ), the two sums cancel each other, at least if the  $\lambda_{\alpha\beta}$  are independent of  $x_\alpha$ . Otherwise there remains a term:

$$\frac{1}{2} \sum_{\alpha\beta} \mathbf{i}_\alpha \mathbf{i}_\beta \frac{\partial \lambda_{\alpha\beta}}{\partial x_1}$$

By writing the tensor of third rank with components  $\partial \lambda_{\alpha\beta} / \partial x_\gamma$  as  $V(\lambda_{\alpha\beta})$ , the following vector equation results:

$$\text{div } \Theta(\mathbf{i}, \mathbf{G}) = \mathbf{G} \text{div } \mathbf{i} - [\mathbf{i} \times \text{curl } \mathbf{G}] + \frac{1}{2} \sum_{\alpha\beta} \mathbf{i}_\alpha \mathbf{i}_\beta V(\lambda_{\alpha\beta}) \quad (13-5)$$

Now we use the continuity equation VI and the fundamental equation X to obtain

$$\text{div } \Theta(\mathbf{i}, \mathbf{G}) = -\mathbf{G} \frac{\partial \rho^s}{\partial t} + \frac{1}{c} [\mathbf{i} \times \mathbf{H}] + \frac{1}{2} \sum_{\alpha\beta} \mathbf{i}_\alpha \mathbf{i}_\beta V(\lambda_{\alpha\beta}) \quad (13-6)$$

Finally remembering IX we write

$$-\mathbf{G} \frac{\partial \rho^s}{\partial t} = -\frac{\partial}{\partial t} (\rho^s \mathbf{G}) + \rho^s \frac{\partial \mathbf{G}}{\partial t} = -\frac{\partial}{\partial t} (\rho^s \mathbf{G}) + \rho^s \mathbf{E}$$

and find in this way that

$$\text{div } \Theta(\mathbf{i}, \mathbf{G}) = \rho^s \mathbf{E} + \frac{1}{c} [\mathbf{i} \times \mathbf{H}] + \frac{1}{2} \sum_{\alpha\beta} \mathbf{i}_\alpha \mathbf{i}_\beta V(\lambda_{\alpha\beta}) - \frac{\partial}{\partial t} (\rho^s \mathbf{G}) \quad (13-7)$$

On the other hand, if we form the Maxwell stress tensors  $T(\mathbf{E})$  and  $T(\mathbf{H})$  for the interior of the superconductor where we do not need to distinguish between  $\mathbf{D}$  and  $\mathbf{E}$  or between  $\mathbf{B}$  and  $\mathbf{H}$ , we have

$$T(\mathbf{E}) = -\Theta(\mathbf{E}, \mathbf{E}), \quad T(\mathbf{H}) = -\Theta(\mathbf{H}, \mathbf{H}) \quad (13-8)$$

Remembering the Maxwell equations I, and IV, it follows from 13-4 that  $-\text{div } \{T(\mathbf{E}) + T(\mathbf{H})\} = \mathbf{E} \text{div } \mathbf{E} - [\mathbf{E} \times \text{curl } \mathbf{E}] + \mathbf{H} \text{div } \mathbf{H} - [\mathbf{H} \times \text{curl } \mathbf{H}]$

$$= \rho \mathbf{E} + \frac{1}{c} [\mathbf{i} \times \mathbf{H}] + \frac{1}{c} \frac{\partial}{\partial t} [\mathbf{E} \times \mathbf{H}] \quad (13-9)$$

<sup>3</sup> See previous footnote.

where  $\rho$  is the total density  $\rho^0 + \rho'$ ,  $\mathbf{i}$  the total current  $\mathbf{i}^0 + \mathbf{i}'$ . Subtracting in eq. 13-7 yields

$$-\operatorname{div} [T(\mathbf{E}) + T(\mathbf{H}) + \Theta(\mathbf{i}, \mathbf{G})] = \rho^0 \mathbf{E} + \frac{1}{c} [\mathbf{i}^0 \times \mathbf{H}] - \frac{1}{2} \sum_{\alpha\beta} \mathbf{i}_\alpha \mathbf{i}_\beta \nabla (\lambda_{\alpha\beta}) + \frac{\partial}{\partial t} \left\{ \frac{1}{c} [\mathbf{E} \times \mathbf{H}] + \rho' \mathbf{G} \right\} \quad (13-10)$$

equation constitutes the momentum law.

In the stationary state  $\mathbf{E}$  and  $\mathbf{i}^0$  vanish (Chap. 7), and for the homogeneous  $\mathbf{i}$  the double sum vanishes. In the stationary state, the Maxwell stresses the magnetic field and the London stresses of the supercurrent result to net force on the interior of a homogeneous superconductor, as was required. The symmetry of the tensor  $\lambda_{\alpha\beta}$  is found to be a necessary and sufficient condition for this. In a time-dependent field the ohmic current mechanism exerts the force  $\rho^0 \mathbf{E} + (1/c) [\mathbf{i}^0 \times \mathbf{H}]$  per unit volume; it acts to change the mechanical momentum density. Moreover, the forces to the three stress tensors produce an increase in the well-known electromagnetic momentum  $(1/c) [\mathbf{E} \times \mathbf{H}]$  and of the momentum density of supercurrent  $\rho' \mathbf{G}$ . (This is why we have called  $\mathbf{G}$  the supermomentum.) Discussion of the double sum in eq. 13-10 is deferred until later. This also shows why we were not permitted to put the superconduction charge density  $\rho'$  equal to zero even in the stationary state where  $\rho$  is zero (see §§. 4 and 5): the momentum  $\rho' \mathbf{G}$  is without doubt always present in the stationary current.

(c) The Maxwell stresses do not act on the surface of a superconductor point in the case (not to be discussed here) that the material immediately on the surface has a dielectric constant or a permeability differing from unity. As all the components of  $\mathbf{E}$  and  $\mathbf{H}$  are continuous across the boundary, according to the boundary conditions of Chap. 3 (c), the tensors  $\lambda$  and  $T(\mathbf{H})$  have equal components on either side of the surface, and have no surface divergence. However, the London tensor  $\Theta(\mathbf{i}, \mathbf{G})$  has a surface divergence because the supercurrent ceases at the surface. Let  $\mathbf{P}_{(n)}$  be this negative surface divergence, the  $n$  referring to the normal of the surface; its components are

$$\mathbf{P}_{(n)} = - \sum_{\beta} \Theta_{\alpha\beta} \cos(n, x_\beta) \quad (13-11)$$

using the definition 13-1 and introducing the unit vector  $n$  in the direction  $n$ , we can write vectorially

$$\mathbf{P}_{(n)} = -\mathbf{i}_n \cdot \mathbf{G} + \frac{1}{2} (\mathbf{i} \cdot \mathbf{G}) n \quad (13-12)$$

is the force exerted by the supercurrent on the surface per unit area. is the only ponderomotive force exerted by the current. Whenever there is no current entering (or leaving) across the surface,  $\mathbf{i} \cdot \mathbf{G}$  is zero, a tension  $\frac{1}{2} (\mathbf{i} \cdot \mathbf{G})$  acts toward the interior. At points where

current enters there is a tangential component of the force due to the first term in 13-12.

In cubic crystals,  $\mathbf{G} = \lambda \mathbf{i}$  has the same direction as  $\mathbf{i}$  everywhere. Then the current streamline is the only intrinsic direction and must be a principal axis of the tensor  $\Theta(\mathbf{i}, \mathbf{G})$ . As can be seen from the equations

$$\Theta_{11} = \frac{1}{2} \lambda \{ \mathbf{i}_1^2 - \mathbf{i}_2^2 - \mathbf{i}_3^2 \}; \quad \Theta_{23} = \Theta_{32} = \lambda \mathbf{i}_2 \mathbf{i}_3 \quad (13-13)$$

this tensor becomes symmetrical. Putting the  $x_1$  axis parallel to the current, the components  $\Theta_{\alpha\beta}$  with mixed suffixes vanish and we get

$$\Theta_{11} = \frac{1}{2} \lambda \mathbf{i}^2, \quad \Theta_{22} = \Theta_{33} = -\frac{1}{2} \lambda \mathbf{i}^2 \quad (13-14)$$

In this case therefore a pressure  $\frac{1}{2} \lambda \mathbf{i}^2$  acts along the current line, and an equal tension perpendicular to it. It manifests itself at the surface where  $\mathbf{i}_n = 0$  as a tension  $\frac{1}{2} \lambda \mathbf{i}^2$  directed toward the interior.

We can illustrate the meaning of the double sum in eq. 13-10 for the cubic crystal case where it reduces to

$$-\frac{1}{2} \mathbf{i}^2 \operatorname{grad} \lambda \quad (13-15)$$

Where two superconductors with different  $\lambda$ 's make contact, the stresses give rise to a force on the boundary. In case the current crosses the boundary perpendicularly,  $(\mathbf{i} \cdot \mathbf{n})_1 = (\mathbf{i} \cdot \mathbf{n})_2$  and eq. 13-15 gives the difference between the two pressures along the current lines:  $\frac{1}{2} \lambda_1 \mathbf{i}^2 (\lambda_1 - \lambda_2)$ . Where, however, the two currents flow parallel to the boundary,  $\lambda_1 (\mathbf{i} \cdot \mathbf{n})_1 = \lambda_2 (\mathbf{i} \cdot \mathbf{n})_2 = C$  according to eq. 3-9, and the integral of eq. 13-15 over the thickness of the boundary layer yields the difference between the two tensions:  $\frac{1}{2} C^2 (1/\lambda_2 - 1/\lambda_1)$ .

In all these cases the force given by eq. 13-15 is directed toward the better superconductor, with the smaller  $\lambda$ .

(d) The stress system assumes a particularly simple form in the fully developed protective layer of a thick cubic crystal conductor. With the  $z$  axis of coordinates along the inner normal, eqs. 7-9 and 7-10 give

$$\mathbf{H}_z = \mathbf{H}, \quad \mathbf{i}_z = \mathbf{i}, \quad \mathbf{H}_x = \mathbf{H}_y = \sqrt{\lambda} \mathbf{i}_x \mathbf{i}_y$$

Therefore in the  $z$  direction the pressure  $\frac{1}{2} \mathbf{H}^2$  of the magnetic field and the tension  $\frac{1}{2} \lambda \mathbf{i}^2$  of the current cancel each other at every point. In the direction of the current, however, the pressure  $\frac{1}{2} \mathbf{H}^2$  and  $\frac{1}{2} \lambda \mathbf{i}^2$  are equal and have to be added together, but because they do not depend on  $z$  they give rise to no resultant force, in agreement with eq. 13-10.

(e) To answer a question remaining from section (a) we now calculate from the London stresses the force exerted on a superconducting cylinder of cubic crystalline material carrying a current  $I$  in a transverse magnetic field  $H^0$ . Figure 13-1 represents a cross section of the cylinder, and if  $H^0$  is in the  $x$  direction, the current produced by this field flows toward the reader at  $a$  and away from the reader at  $b$ . If the current  $I$  flows toward the reader, the current at  $a$  is greater than that at  $b$ . The stronger inward

on at  $a$  and its neighborhood results in a force from  $a$  toward  $b$ , in  $y$  direction in the figure. This force, the current  $I$ , and the field  $H^0$  a right-handed system as they should.

The numerical calculation can be carried out by the methods of Chap. 8 (a) and Chap. 10 (c). From eq. 8-9 the density of the current  $I$  at  $r = R$  is

$$i_r^{(1)} = \frac{c \beta I I_0 (c \beta R)}{2 \pi R I_1 (c \beta R)}$$

The current density due to the field  $H^0$  according to eq. 10-16 is

$$i_r^{(2)} = \frac{2 c H^0 \sin \theta I_1 (c \beta R)}{\sqrt{\lambda} I_0 (c \beta R)}$$

The inward tension therefore has the strength

$$\frac{1}{2} \lambda (i_r^{(1)} + i_r^{(2)})^2$$

If this is multiplied by  $-\sin \theta$ , we obtain its contribution to the total force on the surface  $K_y$ , the value of which is

$$K_y = -\frac{1}{2} R \lambda \int_0^{2\pi} (i_r^{(1)2} + i_r^{(2)2} + 2 i_r^{(1)} i_r^{(2)}) \sin \theta d\theta$$

$$\text{since } \int_0^{2\pi} \sin \theta d\theta = \int_0^{2\pi} \sin^2 \theta d\theta = 0 \text{ and } \int_0^{2\pi} \sin^2 \theta d\theta = \pi, \text{ this reduces}$$

$$K_y = -R \lambda \int_0^{2\pi} i_r^{(1)} i_r^{(2)} \sin \theta d\theta = \frac{I H^0}{c}$$

An example of the tangential component of the force  $K$  would be by a Barlow's wheel made of superconducting cubic crystal material. consists of a circular disk in a magnetic field parallel to its axis that be homogeneous in the absence of the disk; current is supplied in the axis of the disk and is drawn off through a normal conductor perimeter. If the disk is thick compared with the penetration depth, it is distorted by the Meissner effect and considerably increased at periphery, while according to Chap. 7 (g) the field would penetrate a disk relatively undisturbed, assuming it still to be of cubic crystalline

re. above stresses act on the two circular faces of the disk. Because parallel to the axis they produce no angular momentum. However, a point where the current leaves the disk there is a tangential current

$i_\theta$  flowing along the periphery which is proportional to  $H^0$  and protects the interior of the (thick) superconductor from the field. At the point where the current leaves, there is a tangential force  $\Theta_\theta = \lambda i_r i_\theta$  that does produce angular momentum. The calculation shows that with a thin disk the force has the same value as for a normal conductor, while with a thick disk it has the same direction but is much weaker.\*

The reality of the Maxwell stresses in empty space is vouchsafed by the principle of relativity. In so far as the energy density has reality in all inertial systems connected by a Lorentz transformation, the same reality must be ascribed to the stress components that are transformed along with this energy density and form with it a "world tensor." It is difficult to believe that this does not also hold for the Maxwell stresses. However, it is not inconceivable that the London stresses are purely a convenient mathematical fiction. In what follows we assume the contrary.

(g) Because in the above examples the net force and the torque are acting on an essentially rigid body, we could have started from the external magnetic stresses  $T(\mathbf{H})$  instead of from the London stresses in the interior; which stresses exist in the interior is of no importance for such a calculation so long as all the stress tensors are symmetrical.

In order to carry through this alternative, we recall the two well-known integral theorems of the tensor theory; it is possible by partial integration to transform certain volume integrals of an arbitrary asymmetrical tensor  $t_{\alpha\beta}$  into surface integrals. Let  $n$  again mean the inner normal, then we have first

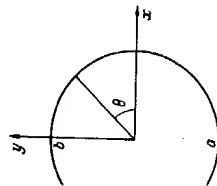
$$\int \left[ \frac{\partial t_{11}}{\partial x_1} + \frac{\partial t_{12}}{\partial x_2} + \frac{\partial t_{13}}{\partial x_3} \right] d\tau = - \int [t_{11} \cos(n, x_1) + t_{12} \cos(n, x_2) + t_{13} \cos(n, x_3)] d\sigma \quad (13-16)^*$$

and secondly,

$$\begin{aligned} \int \left\{ x_2 \left( \frac{\partial t_{31}}{\partial x_1} + \frac{\partial t_{32}}{\partial x_2} + \frac{\partial t_{33}}{\partial x_3} \right) - x_3 \left( \frac{\partial t_{21}}{\partial x_1} + \frac{\partial t_{22}}{\partial x_2} + \frac{\partial t_{23}}{\partial x_3} \right) \right\} d\tau = \\ = - \int \left\{ x_2 [t_{31} \cos(n, x_1) + t_{32} \cos(n, x_2) + t_{33} \cos(n, x_3)] - x_3 [t_{21} \cos(n, x_1) + \right. \\ \left. + t_{22} \cos(n, x_2) + t_{23} \cos(n, x_3)] \right\} d\sigma + \int (t_{33} - t_{22}) d\tau \quad (13-17) \end{aligned}$$

\*W. Heisenberg and M. v. Laue, *Z. Physik*, 124, 514 (1948). With regard to the present state of our knowledge about supercurrents and surface phenomena, one might perhaps doubt whether the torque is acting on the disk itself or on the normally conducting wire that leads the current out of the disk. The phenomenological theory described here cannot answer this question, but we could imagine the leads replaced by a cold emission from the periphery through the surrounding space when it could conceivably be decided experimentally whether or not the torque acts on the wheel.

\* In this and subsequent formulas  $d\sigma$  is not a vector.



force per unit area on any surface due to the tensor  $T(\mathbf{H})$  now has components

$$F_{na} = \sum_{\beta} T_{a\beta} \cos(n, x_{\beta}) \quad (13-18)$$

which can be written together in vector form:<sup>5</sup>

$$\mathbf{F}_n = -\mathbf{H}_n \mathbf{H} + \mathbf{H}^2 \mathbf{n} \quad (13-19)$$

again the unit vector normal).

The difference in sign between the right-hand sides of eqs. 13-18 and 11 is due to the fact that the Maxwell stresses we are discussing here outside the space element, whereas the London stresses are inside it. Resultant force on this element is, according to eq. 13-16,

$$-\int \operatorname{div} T(\mathbf{H}) d\tau = \int \mathbf{F}_n d\sigma \quad (13-20)$$

the torque due to the Maxwell stresses is:

$$-\int [\mathbf{r} \times \operatorname{div} T(\mathbf{H})] d\tau = \int [\mathbf{r} \times \mathbf{F}_n] d\sigma \quad (13-21)^6$$

By using eq. 13-20 one can easily calculate from  $\mathbf{F}_n$ , e. g., the force  $\int \mathbf{H}^0$  acting on the cylinder carrying a current in a magnetic field (cf.).

We now want to find the conditions under which the net force and the torque due to the Maxwell stresses in the outside space coincide with the force and the torque due to the London stresses in the interior.

The volume integral for the Maxwell stresses on the right-hand side of eq. 13-17 vanishes because the tensor  $T(\mathbf{H}) = -\Theta(\mathbf{H}, \mathbf{H})$  is metrical, according to eq. 13-2. It also vanishes for the tensor  $\Theta(\mathbf{H}, \mathbf{G})$  in a cubic crystalline superconductor because in this case  $\mathbf{G} = \lambda \mathbf{H}$ . Before integrating eq. 13-11 over the volume of the superconductor, g. eqs. 13-16 and 13-17, we conclude that

$$-\int \operatorname{div} \Theta(\mathbf{H}, \mathbf{G}) d\tau = -\int \mathbf{K}_n d\sigma \quad (13-22)$$

$$-\int [\mathbf{r} \times \operatorname{div} \Theta(\mathbf{H}, \mathbf{G})] d\tau = -\int [\mathbf{r} \times \mathbf{K}_n] d\sigma \quad (13-23)$$

the homogeneous superconductor in a stationary state we have, according to eq. 13-10,  $\operatorname{div} T(\mathbf{H}) = -\operatorname{div} \Theta(\mathbf{H}, \mathbf{G})$ . Therefore

$$\int \mathbf{F}_n d\sigma = \int \mathbf{K}_n d\sigma, \quad \int [\mathbf{r} \times \mathbf{F}_n] d\sigma = \int [\mathbf{r} \times \mathbf{K}_n] d\sigma \quad (13-24)$$

net resultant force acting on an arbitrary superconductor can be calculated equally well either from the Maxwell stresses in the outside space or from the London stresses in the interior. The two methods give

<sup>5</sup>Because according to eqs. 13-8 and 13-1,  $T_{a\beta}(\mathbf{H}) = -H_a H_{\beta} + \frac{1}{2} \delta_{a\beta} H^2$ .

<sup>6</sup> $\mathbf{r}$  is the vector whose components are the  $x_i$ .

the same results for the torque of the force only if the superconductor is of cubic crystal material. This always is true, although the separate forces  $\mathbf{F}_n$  and  $\mathbf{K}_n$  may have the same value, namely,  $\mathbf{F}_n = \mathbf{K}_n = \frac{1}{2} \mathbf{H}^2 \mathbf{n}$ , only for thick superconductors (compare eqs. 13-12, 13-19, and 7-37) and where no current is entering or leaving the superconductor.

However, when in Chap. 17 we calculate the work performed by the magnetic field during an arbitrary displacement of the phase boundary between normal and superconducting material, we have to start from the forces  $\mathbf{K}_n$  due to the London stresses, because they alone yield the actual force on every element of the surface.

(h) We still have to consider the term  $\int (t_{32} - t_{23}) d\tau$  in eq. 13-17 as applied to the tensor  $\Theta(\mathbf{H}, \mathbf{G})$ . In the first place this equation, the other terms of which represent torques, shows that  $t_{23} - t_{32}$  is the  $x$  component of a polar vector. We therefore introduce the vector  $\theta$  with the components

$$\theta_1 = \Theta_{23} - \Theta_{32}, \quad \theta_2 = \Theta_{31} - \Theta_{13}, \quad \theta_3 = \Theta_{12} - \Theta_{21} \quad (13-25)$$

which according to eq. 13-2 we can also write vectorially as

$$\theta = [\mathbf{G} \times \mathbf{H}] \quad (13-26)$$

Equation 13-23 obviously has to be supplemented to read

$$-\int [\mathbf{r} \times \operatorname{div} \Theta(\mathbf{H}, \mathbf{G})] d\tau = -\int [\mathbf{r} \times \mathbf{K}_n] d\sigma + \int \theta d\tau \quad (13-27)$$

We can apply this equation not only to the whole volume of the superconductor but also to any part of it, provided only we keep in mind that in this case the forces  $\mathbf{K}_n$  are not effective, but are completely compensated by the London stresses from outside the region of integration. Equation 13-27 therefore states: The London stresses in a noncubic crystal superconductor produce a torque  $\theta$  per unit volume. Because of the equality between action and reaction the material, in the stationary state, has to exert a torque  $\theta' = -\theta$  on the superconduction mechanism. This result at first seems most surprising.

In classical mechanics there are already cases where a torque is necessary to maintain uniform motion.

For example, a rigid body moving through liquid thrusts the latter to one side, in the absence of special symmetry conditions, and an impulse component perpendicular to the velocity  $\mathbf{v}$  is associated with the motion of the body. As this impulse is displaced along with the body, the angular momentum is changing by  $[\mathbf{v} \times \mathbf{G}]$  per unit time, where  $\mathbf{G}$  represents the momentum of the body. If a torque of this direction and magnitude did not act on the body it would not be able to persist in its uniform motion. See Fig. 13-2.

Section (b) showed us that a momentum  $\rho^2 \mathbf{G}$  per unit volume is associated with the supercurrent. The concept of a velocity  $\mathbf{v}$  of the super-

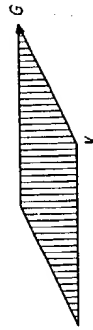


Fig. 13-2. The shaded area represents the vector product  $[\mathbf{v} \times \mathbf{G}]$  i. e., the increase in angular momentum per unit time.

it is alien to the phenomenological theory. However, in so far as any meaning at all, it certainly has the value given by  $\rho' \mathbf{v} = \mathbf{i}$ , the required torque per unit volume becomes

$$\theta' = [\mathbf{v} \times \rho' \mathbf{G}] = [\mathbf{i} \times \mathbf{G}]$$

is actually is equal to  $-\theta$ .  
 a combination of eqs. 13-27 and 13-10 gives for the whole superconductor

$$\int [\mathbf{r} \times \mathbf{F}_s] d\sigma = \int [\mathbf{r} \times \mathbf{K}_s] d\sigma + \int \theta' d\tau \quad (13-28)$$

1 of the second equation of 13-24.

2 torque due to the Maxwell stresses in outside space,  $\int [\mathbf{r} \times \mathbf{F}_s] \cdot d\sigma$  is moment of all the forces acting on the superconductor from outside, to increase the mechanical angular momentum of the superconductor by other bodies rigidly connected with it) by the amount  $\int [\mathbf{r} \times \mathbf{K}_s] \cdot d\sigma$ ; according to this equation angular momentum is also imparted to the conducting mechanism.

The results of this chapter concerning ponderomotive forces and due to the field are so important for the further development of the that we wish to confirm them in the next chapter by expressing them is of an electrodynamic potential, at least for the stationary case. Give this potential itself by a plausible generalization of the usual al of the Maxwell theory.

## CHAPTER 14

### The Electrodynamic Potential

We shall prove the following theorem with the unimportant ion that only one superconductor is situated in the field, and the important restriction that no ohmic current is supplied: In any quasi-ary change of the field, occurring as a consequence of displacements ter, the work  $\partial A$  performed by the field is equal to the decrease of trodynamic potential  $-\partial V$  defined by

$$V = \frac{SI}{c} - \int_V \left\{ \frac{1}{2} \mu \mathbf{H}^2 + (\mathbf{M} \cdot \mathbf{H}) + \frac{1}{2} (\mathbf{i} \cdot \mathbf{G}) \right\} d\tau \quad (14-1)$$

chap. 12,  $I$  is the current flowing in the superconductor when the in the form of a ring,  $S$  is the time invariant period of the super-ion potential  $\Psi$ ; if the superconductor is singly connected the

compare Von Laue reference  $\epsilon$  and  $f$  in footnote 2, Chapter 3.

first term is absent. The integration has to be extended over the whole of space (as indicated by the suffix  $V$ ). In the term  $(\mathbf{M} \cdot \mathbf{H})$  the integration is taken only over the volume of the permanent magnets, in the term  $\frac{1}{2} (\mathbf{i} \cdot \mathbf{G})$  only over the volume of the superconductor: these two volumes are mutually exclusive, and the observation that no ferromagnetics ever become superconducting is therefore significant for the following proof. Electric field vectors do not appear because of our assumption that at every instant the state is infinitesimally near to a stationary state.

Let the material displacement be  $\partial \mathbf{u}$ , a continuous vector function of position. The proof of the above theorem is effected as soon as we can express the decrease in potential in the form

$$-\partial V = \int_V \left\{ (\mathbf{K} \cdot \partial \mathbf{u}) + \frac{1}{4} (\theta \cdot \text{curl } \partial \mathbf{u}) \right\} d\tau \quad (14-2)$$

where  $\mathbf{K}$  means the force per unit volume determined by the well-known electrodynamic laws, and  $\theta$  is the torque given by eq. 13-26. In other words we must show that the right-hand side of this expression is the work  $\partial A$  done by the field. The boundary conditions are that all material constants, including  $\lambda_{\theta}$  and  $\mu$  do not change their values at any material point, furthermore that the ohmic current flows through any material surface with the same strength  $\int \mathbf{i}_n \cdot d\sigma'$  before and after the displacement, and also that the permanent magnetism  $\int \mathbf{M}_n \cdot d\sigma'$  remains unchanged.<sup>2</sup> We shall therefore have

$$\partial \int_V \mathbf{i}_n \cdot d\sigma' = 0, \quad \partial \int \mathbf{M}_n \cdot d\sigma' = 0 \quad (14-3)$$

We assume the condition of the constant ohmic current strength to be realized by arranging for suitable changes of the electromotive forces to compensate all changes of induction due to the displacements. We cannot introduce such a condition for the annular current in a superconductor. For this current it is the potential period  $S$  (Chap. 12) and not the current strength that remains unchanged, and for the current density here we have eq. 12-10,

$$c \mathbf{G} + \mathbf{A} = \text{grad } \Psi \quad (14-4)$$

(b) To formulate the assumptions under discussion mathematically we use at first some well-known equations. If  $\partial \mu$  means the change of the parameter  $\mu$  at a material point,  $\partial \mu$ , the change at a point fixed in space, the following relation holds:

$$\partial \mu = \partial \mu + (\partial \mathbf{u} \cdot \text{grad } \mu)$$

As  $\partial \mu$  shall be zero, we have to put

$$\partial \mu = -(\partial \mathbf{u} \cdot \text{grad } \mu) \quad (14-5)$$

Furthermore, the change of flux of an arbitrary vector through a material surface integrates to

$$\delta \int \mathbf{K}_n \cdot d\sigma' = \int \{ \partial \mathbf{K} + \partial \mathbf{u} \text{ div } \mathbf{K} - \text{curl } [\partial \mathbf{u} \times \mathbf{K}] \} \cdot d\sigma'$$

<sup>2</sup>  $d\sigma'$ , in contrast to  $d\sigma$ , is a surface element participating in the displacement.

before if we remember that here the stationary state means  $\text{div } \mathbf{i}^0 = 0$ , conditions 14-3 yield

$$\partial \mathbf{M} = \text{curl} [\partial \mathbf{u} \times \mathbf{i}^0] \quad (14-6)$$

$$\partial \mathbf{M} = -(\text{div } \mathbf{M}) \partial \mathbf{u} + \text{curl} [\partial \mathbf{u} \times \mathbf{M}] \quad (14-7)$$

ough the above considerations are based on well-known theorems<sup>3</sup> we have to leave the proof of the next equation to the Appendix, namely that under the condition that the  $\lambda_{\alpha\beta}$  do not change at any point, the changes  $\partial \lambda_{\alpha\beta}$  at a fixed point in space satisfy the equation

$$\sum_{\alpha\beta} \mathbf{i}_{\alpha} \mathbf{i}_{\beta} \partial \lambda_{\alpha\beta} = -\frac{1}{2} \sum_{\alpha\beta} \mathbf{i}_{\alpha} \mathbf{i}_{\beta} (\partial \mathbf{u} \cdot \nabla \lambda_{\alpha\beta}) + \frac{1}{2} (\text{curl } \partial \mathbf{u} \cdot [\mathbf{G} \times \mathbf{i}]) \quad (14-8)$$

obvious that throughout the superconductor

$$\text{div } \mathbf{i} = 0 \quad (14-9)$$

at its boundary

$$\mathbf{i}_{\alpha} = 0 \quad (14-10)$$

like into account only one surface of discontinuity, namely the surface of the superconductor, and assume all other transitions to be continuous. The permanent magnetization  $\mathbf{M}$  must go continuously to zero from the interior of a permanent magnet; the actual conditions can be taken care of afterwards by going to the limit.

We proceed to the proof of eq. 14-2. According to eq. 14-1 we have

$$-\partial V = -\frac{S}{c} \partial I + \partial \int_V \left[ \frac{1}{2} \mu \mathbf{H}^2 + (\mathbf{M} \cdot \mathbf{H}) + \frac{1}{2} (\mathbf{i} \cdot \mathbf{G}) \right] d\tau$$

right-hand side can be split into six terms of the following type:

$$-\partial V = \sum_{n=1}^5 \partial I_n - \frac{S}{c} \partial I$$

$$\partial I_1 = \int_V (\mathbf{B} \cdot \partial \mathbf{H}) d\tau$$

$$\partial I_2 = \int_V (\mathbf{H} \cdot \partial \mathbf{M}) d\tau$$

$$\partial I_3 = \frac{1}{2} \int_V \mathbf{H}^2 \partial \mu d\tau$$

$$\partial I_4 = \int_V (\mathbf{G} \cdot \partial \mathbf{i}) d\tau$$

$$(14-11)^4$$

<sup>3</sup>for example, Margenau and Murphy, *Mathematics of Physics and Chemistry*, Nostrand, New York Chapter IV.

<sup>4</sup>before the suffixes  $s$  and  $P$  mean that the integration has to extend over the conductor or the permanent magnets respectively.

$$\partial I_5 = \frac{1}{2} \int_V \mathbf{i}_{\alpha} \mathbf{i}_{\beta} \partial \lambda_{\alpha\beta} d\tau$$

This is because

$$\frac{1}{2} \partial (\mathbf{i} \cdot \mathbf{G}) = \frac{1}{2} \partial \left( \sum_{\alpha\beta} \mathbf{i}_{\alpha} \mathbf{i}_{\beta} \lambda_{\alpha\beta} \right) = \sum_{\alpha\beta} \lambda_{\alpha\beta} \mathbf{i}_{\alpha} \partial \mathbf{i}_{\beta} + \frac{1}{2} \sum_{\alpha\beta} \mathbf{i}_{\alpha} \mathbf{i}_{\beta} \partial \lambda_{\alpha\beta}$$

and

$$\frac{1}{2} \int_V \partial (\mathbf{i} \cdot \mathbf{G}) d\tau = \partial I_4 + \partial I_5$$

We now use eq. 12-1, the theorem 5-1, and the fundamental equation II to rewrite  $\partial I_1$  in the form

$$\partial I_1 = \int_V (\text{curl } \mathbf{A} \cdot \partial \mathbf{H}) d\tau = \int_V (\text{curl } \partial \mathbf{H} \cdot \mathbf{A}) d\tau = \frac{1}{c} \int_V [(\mathbf{A} \cdot \partial \mathbf{i}^0) + (\mathbf{A} \cdot \partial \mathbf{i})] d\tau$$

Consequently by eq. 14-4,

$$\partial I_1 + \partial I_4 = \frac{1}{c} \left[ \int_V (\mathbf{A} \cdot \partial \mathbf{i}^0) d\tau + \int_S (\text{grad } \Psi \cdot \partial \mathbf{i}) d\tau \right]$$

However, partial integration over the superconductor yields

$$\frac{1}{c} \int_V (\text{grad } \Psi \cdot \partial \mathbf{i}^0) d\tau = -\frac{1}{c} \int_S \Psi \text{div } \partial \mathbf{i} d\tau - \frac{1}{c} \int_V \Psi \partial \mathbf{i} \cdot d\sigma$$

The first term vanishes because of eq. 14-9, and the surface makes no contribution because of eq. 14-10. But with a doubly connected body, a cut  $Q$  makes a contribution to the surface integral (compare eq. 12-17):

$$-\frac{1}{c} \int_Q \Psi \partial \mathbf{i} \cdot d\sigma = \frac{1}{c} (\Psi_2 - \Psi_1) \partial I = \frac{S}{c} \partial I$$

The sign is determined by the convention of Chap. 12 that a positive current flows through the cut in the direction  $2 \rightarrow 1$ . On the other hand, according to eqs. 14-6 and 12-1:

$$\begin{aligned} \frac{1}{c} \int_V (\mathbf{A} \cdot \partial \mathbf{i}^0) d\tau &= \frac{1}{c} \int_V (\mathbf{A} \cdot \text{curl} [\partial \mathbf{u} \times \mathbf{i}^0]) d\tau \\ &= \frac{1}{c} \int_V (\mathbf{B} \cdot [\partial \mathbf{u} \times \mathbf{i}^0]) d\tau = \frac{1}{c} \int_V (\partial \mathbf{u} \cdot [\mathbf{i}^0 \times \mathbf{B}]) d\tau \end{aligned}$$

Consequently we have

$$\partial I_1 + \partial I_4 = \frac{S}{c} \partial I + \int_V (\partial \mathbf{u} \cdot [\mathbf{i}^0 \times \mathbf{B}]) d\tau \quad (14-12)$$

using eqs. 13-26 and 14-8 we can rewrite

$$\partial I_3 = \frac{1}{2} \int_V \left[ - \sum_{\alpha\beta} \mathbf{i}_\alpha \mathbf{i}_\beta \nabla \lambda_{\alpha\beta} + (\theta \cdot \text{curl } \partial \mathbf{u}) \right] d\tau \quad (14-13)$$

Moreover, by eq. 14-7, the theorem 5-1, and the fundamental equation remembering that the supercurrent  $\mathbf{i}^0$  is absent from the interior of the permanent magnets) we get

$$\begin{aligned} \partial I_2 &= \int_V \left\{ \mathbf{H} \cdot (\text{curl } [\partial \mathbf{u} \times \mathbf{M}] - \partial \mathbf{u} \text{ div } \mathbf{M}) \right\} d\tau \\ &= \int_V \left\{ \frac{1}{c} ([\partial \mathbf{u} \times \mathbf{M}] \cdot \mathbf{i}^0) - (\partial \mathbf{u} \cdot \mathbf{H} \text{ div } \mathbf{M}) \right\} d\tau \\ &= \int_V \left\{ - \frac{1}{c} (\partial \mathbf{u} \cdot [\mathbf{i}^0 \times \mathbf{M}]) - (\partial \mathbf{u} \cdot \mathbf{H} \text{ div } \mathbf{M}) \right\} d\tau \end{aligned} \quad (14-14)$$

it follows from eq. 14-5 that

$$\partial I_3 = - \frac{1}{2} \int_V \mathbf{H}^2 (\partial \mathbf{u} \cdot \text{grad } \mu) d\tau \quad (14-15)$$

ling together eqs. 14-12 to 14-15 and using eq. 14-11 we obtain

$$- \partial V = \int_V \left\{ (\mathbf{K} \cdot \partial \mathbf{u}) + \frac{1}{2} (\theta \cdot \text{curl } \partial \mathbf{u}) \right\} d\tau \quad (14-16)$$

ie value of the vector  $\mathbf{K}$  given by

$$\frac{1}{c} [\mathbf{i}^0 \times \mu \mathbf{H}] - \mathbf{H} \text{ div } \mathbf{M} - \frac{1}{2} \mathbf{H}^2 \text{ grad } \mu - \frac{1}{2} \sum_{\alpha\beta} \mathbf{i}_\alpha \mathbf{i}_\beta \nabla \lambda_{\alpha\beta} \quad (14-17)$$

the most general expression for the force exerted by a stationary ic field on a unit volume of matter. The first term represents the of the field on ohmic current, the second term is the effect on the of permanent magnetic charges as measured by  $-\text{div } \mathbf{M}$ , the the equally familiar force on regions of magnetic inhomogeneity, rth is the force on an inhomogeneous superconductor appearing in 10. Equations 14-16 and 14-17 contain therefore the proof of the statement that  $\mathbf{K} = 0$  for the homogeneous superconductor, for eq. 13-10  $\mathbf{K} = 0$ .

The theorem  $\partial A = -\partial V$  comes from the Maxwell theory, and nition 14-1 is simply a plausible extension of the definition of that That we have arrived at exactly the same conclusions about the and the torque  $\theta$  by a line of reasoning that avoids the stress used in Chap. 13 on the argument about the London stresses seems be a valuable confirmation of the essential truth of that theory. ion, the observation that ferromagnetics are unable to show super-

conductivity appears in a new light. Otherwise we would have found in eq. 14-14 another term

$$- \frac{1}{c} (\partial \mathbf{u} \cdot [\mathbf{i}^0 \times \mathbf{M}])$$

also entering the expression for the force  $\mathbf{K}$ , and this would have been in conflict with the fact that the existence of persistent currents demands that  $\mathbf{K}$  be zero in a homogeneous superconductor. It seems as though permanent magnetism and superconductivity are mutually exclusive not only in the temperature ranges that happen to have been observed to date, but also fundamentally so.

(e) According to eq. 12-21 the total (available) energy of the field is

$$U = \frac{1}{2} \int_V \left\{ \mu \mathbf{H}^2 + (\mathbf{i} \cdot \mathbf{G}) \right\} d\tau = \frac{1}{2c} \left\{ \int_V \mathbf{S} \cdot \mathbf{I} + \int_V (\mathbf{A} \cdot \mathbf{i}^0) d\tau \right\} - \frac{1}{2} \int_V (\mathbf{H} \cdot \mathbf{M}) d\tau \quad (14-18)$$

and so according to eq. 14-1,

$$V = \frac{1}{2c} \left[ \int_V \mathbf{S} \cdot \mathbf{I} - \int_V (\mathbf{A} \cdot \mathbf{i}^0) d\tau \right] - \frac{1}{2} \int_V (\mathbf{H} \cdot \mathbf{M}) d\tau \quad (14-19)$$

If the field is produced only by an annular current  $I$  and permanent magnets, then  $V = U$  and the work  $\partial A = -\partial U$ . Conversely if the field is produced by ohmic currents,  $V = -U$  and  $\partial A = \partial U$ . The amount of work  $2 \partial A$  has then to be performed by the electromotive forces keeping the currents constant. This second point differs from the corresponding theorem of the Maxwell theory in that here superconductors (but with no annular currents) are permitted to be in the field.

Eliminating the term  $\mathbf{S} \cdot \mathbf{I}/c$  from eq. 14-1 by means of eq. 12-19 we get a new expression for  $V$  of which we shall make immediate use, namely,

$$V = \frac{1}{c} \int_V (\mathbf{A} \cdot \mathbf{i}) d\tau + \frac{1}{2} \int_V (\mathbf{i} \cdot \mathbf{G}) d\tau - \int_V \left[ \frac{1}{2} \mu \mathbf{H}^2 + (\mathbf{M} \cdot \mathbf{H}) \right] d\tau \quad (14-20)$$

(f) With the help of the potential  $V$  we shall now confirm the theorem of Chap. 13 (c) that the surface of the superconductor experiences an inward pull  $\frac{1}{2} (\mathbf{i} \cdot \mathbf{G})$  at all points where there is no current entering or leaving. For this purpose we ignore all displacements of matter, but displace the boundary between a superconducting and a chemically identical normal conducting phase in such a way that every surface element  $d\sigma$  suffers a displacement  $\partial \mathbf{u}$  normal to  $d\sigma$ . We take  $\partial \mathbf{u}$  to be positive if  $d\sigma$  moves toward the interior of the superconductor. If before the displacement the superconducting phase occupied the region  $s$ , afterwards it occupies the smaller region  $s'$ . A finite change therefore takes place in the layer  $s \rightarrow s'$ ; supercurrent and supermomentum suddenly drop to zero. But as this layer is infinitely thin, the effects of this change at all other points in space is infinitesimal. In general  $\mu$  and  $\lambda_{\alpha\beta}$  do not change at all, and the same is true of the current density  $\mathbf{i}^0$ , as we shall again keep the ohmic currents constant.

Starting from eq. 14-20 we split the change  $-\partial V$  into five parts:

$$\begin{aligned}\partial V &= \sum_{k=1}^5 \partial I_k \\ \partial I_3 &= \int_V (\mathbf{B} \cdot \partial \mathbf{H}) d\tau \\ I_1 &= -\frac{1}{c} \int_V \partial (\mathbf{A} \cdot \mathbf{i}) d\tau \\ \partial I_4 &= \int_{s_1-s'} (\mathbf{A} \cdot \mathbf{i}) d\tau \\ I_2 &= -\int_V (\mathbf{G} \cdot \partial \mathbf{i}) d\tau \\ \partial I_5 &= \frac{1}{2} \int_{s_1-s'} (\mathbf{i} \cdot \mathbf{G}) d\tau\end{aligned}\quad (14-21)$$

transformation proceeds as follows. First, by eq. 14-4 we have

$$\partial I_1 + \partial I_2 = -\frac{1}{c} \int_V [(\text{grad } \Psi \cdot \partial \mathbf{i}) + (\mathbf{i} \cdot \partial \mathbf{A})] d\tau$$

in spite of the infinitesimal  $\partial \mathbf{H}$  in the layer  $s-s'$  by which the conductor is reduced,  $\text{curl } \partial \mathbf{H} = -\mathbf{i}/c$  is finite, but  $\partial \mathbf{i}^0 = 0$  where; remembering this and using eq. 12-1 and the theorem 5-1 follows that

$$\partial I_3 = \frac{1}{c} \left[ \int_V (\mathbf{A} \cdot \partial \mathbf{i}) d\tau - \int_{s-s'} (\mathbf{A} \cdot \mathbf{i}) d\tau \right]$$

adding up  $\partial I_1$  to  $\partial I_3$  the contributions of the layer  $s-s'$  cancel. Again using eq. 14-4 there remains

$$\begin{aligned}\sum_{k=1}^4 \partial I_k &= \frac{1}{c} \int_V [(\mathbf{A} - \text{grad } \Psi) \cdot \partial \mathbf{i}] - (\mathbf{i} \cdot \partial \mathbf{A})] d\tau \\ &= -\int_V \left\{ (\mathbf{G} \cdot \partial \mathbf{i}) + \frac{1}{c} (\mathbf{i} \cdot \partial \mathbf{A}) \right\} d\tau\end{aligned}$$

because of the symmetry of the tensor  $\lambda_{\alpha\beta}$ , which enters once more in important condition, we have

$$(\mathbf{G} \cdot \partial \mathbf{i}) = \sum_{\alpha\beta} \lambda_{\alpha\beta} i_\alpha \partial i_\beta = \sum_{\alpha\beta} \lambda_{\alpha\beta} \partial i_\alpha i_\beta = (\mathbf{i} \cdot \partial \mathbf{G})$$

so from eqs. 14-4 and 14-9 and the constancy of  $S = \Psi_2 - \Psi_1$  we

$$\begin{aligned}\sum_{k=1}^4 \partial I_k &= -\int_V \left( \mathbf{i} \cdot \partial \left[ \mathbf{G} + \frac{\mathbf{A}}{c} \right] \right) d\tau = -\frac{1}{c} \int_V (\mathbf{i} \cdot \text{grad } \partial \Psi) d\tau \\ &= \frac{1}{c} \int_V \Psi \text{div } \mathbf{i} d\tau - I \partial (\Psi_2 - \Psi_1) = 0\end{aligned}\quad (14-22)$$

There remains only the term  $\partial I_5$  in eq. 14-21 to be considered. In the layer  $s-s'$  however, putting the volume element  $d\tau = d\sigma' \cdot d\mathbf{u}$  we get by surface integration

$$\partial A = -\partial V = \frac{1}{2} \int_V (\mathbf{i} \cdot \mathbf{G}) \partial \mathbf{n} \cdot d\sigma' \quad (14-23)$$

From this we deduce that  $\frac{1}{2} (\mathbf{i} \cdot \mathbf{G})$  is in fact the pull acting over the element  $d\sigma'$  toward the interior of the superconductor.

(g) From the section (f) we can also make the following deduction. Given the relative positions of all bodies, the ohmic currents in them, the permanent magnetism, and the potential "period"  $S$  of all possible annular currents which may eventually appear, the stationary field adjusts itself to minimize the electrodynamic potential.

If we disregard the displacements  $\partial \mathbf{u}$ , the integrals  $\partial I_4$  and  $\partial I_5$  in eq. 14-21 vanish for every virtual displacement of the field. Then eq. 14-22 gives

$$-\partial V = \sum_{k=1}^3 I_k = 0$$

If there is no ohmic current contributing to the field then  $V = U$  according to section (e). The field adjusts itself to minimize the free energy. Also a persistent current by itself corresponds to a minimum of the free energy, of course with the boundary condition that the potential "period"  $S$  be given. Without such a condition the law of the minimum free energy cannot be proved.

## CHAPTER 15

## Electric Waves in Superconductors with Cubic Crystal Structure

(a) According to the fundamental equation IX changes in time always produce an electric intensity  $\mathbf{E}$  in a superconductor; this in turn produces an ohmic current density  $\mathbf{j}^0$  in addition to the supercurrent, and also Joule heat according to the energy equation 5-6. This is the fundamental difference from static fields. To describe periodic waves, in what follows we always use complex expressions for the field strengths and all quantities linearly related to them. The waves will be designated by their angular frequency  $\omega$ , the numerical frequency  $\nu$  being  $\omega/2\pi$ . All the complex expressions are taken proportional to  $e^{i\nu t}$ .

It follows from VII a and IX for cubic crystal superconductors that

$$\mathbf{j}^0 = \sigma \mathbf{E} = \omega \sigma \lambda \mathbf{i} e^{i\nu t/2} \quad (15-1)$$



supercurrent  $\mathbf{i}$  is therefore lagging in phase by a quarter period behind ohmic current and the field strength  $\mathbf{E}$ . For the ratio of the amplitudes of the two waves we have

$$\frac{|\mathbf{i}^0|}{|\mathbf{i}|} = \omega \sigma \lambda \quad (15-2)$$

greater  $\omega$  the greater the influence of  $\mathbf{i}^0$  compared with  $\mathbf{i}$ . The pure ohmic  $\omega \sigma \lambda$  which we encounter here for the first time, will play a fundamental role in the ensuing calculations. The total current density connected with the field strength by the relation

$$\mathbf{i} = \mathbf{i}^0 + \mathbf{i}^1 = \mathbf{E} \frac{\omega \sigma \lambda - i}{\omega \lambda} \\ = \mathbf{E} \frac{1 + i \omega \sigma \lambda}{i \omega \lambda} \quad (15-3)$$

b) Because of the inevitable production of Joule heat a progressive wave in a superconductor is damped just as in a normal conductor. For a polarized wave progressing in the  $z$  direction we write

$$\mathbf{E}_x = E_0 \exp i \omega \left\{ t - \frac{(n - i \kappa) z}{c} \right\}, \quad \mathbf{E}_y = \mathbf{E}_z = 0 \quad (15-4)$$

satisfies the condition  $\text{div } \mathbf{E} = 0$ . According to the fundamental equation I it follows from this that

$$0 = \mathbf{H}_y = (n - i \kappa) E \exp i \omega \left\{ t - \frac{(n - i \kappa) z}{c} \right\}, \quad \mathbf{H}_x = 0 \quad (15-5)$$

sequently for waves in a superconductor the electric field strength, magnetic field strength, and direction of propagation are perpendicular to each other and form in this order a right-handed system, as is otherwise to be the case. However, unlike the behavior of waves in a non-conductor,  $\mathbf{E}$  and  $\mathbf{H}$  do not oscillate in phase,  $\mathbf{E}$  in general lagging in phase and  $\mathbf{H}$ . The amplitude decreases with increasing  $z$  by the factor  $e^{-\omega \sigma \lambda z/c}$ , energy density by  $e^{-2\omega \sigma \lambda z/c}$ .  $\kappa$  is called the extinction coefficient, a refractive index. Both are pure numbers and functions of  $\omega$ . Inserting the value of  $\mathbf{E}$  from eq. 15-4 in the telegrapher's equation  $\Delta \mathbf{E} = 0$  (compare Chap. 6; it is equally possible to insert the value from eq. 15-5 in  $\Delta \mathbf{H} = 0$ ), because

$$\Delta \mathbf{E} = \Delta \mathbf{E} - \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = \frac{\sigma}{c^2} \frac{\partial \mathbf{E}}{\partial t} - \frac{\mathbf{E}}{\lambda^2 c^2}$$

obtains the relation

$$(n - i \kappa)^2 = \frac{(\omega^2 \lambda^2 - 1 - i \omega \sigma \lambda)}{\omega^2 \lambda^2} \quad (15-6)$$

two real numbers  $n$  and  $\kappa$  are determined by

$$n^2 = \frac{1}{2} \frac{[(\omega^2 \lambda^2 - 1) + \sqrt{(\omega^2 \lambda^2 - 1)^2 + (\omega \sigma \lambda)^2}]}{\lambda \omega^2} \\ \kappa^2 = \frac{1}{2} \frac{[-(\omega^2 \lambda^2 - 1) + \sqrt{(\omega^2 \lambda^2 - 1)^2 + (\omega \sigma \lambda)^2}]}{\lambda \omega^2} \quad (15-7)$$

If  $\omega^2 \lambda^2 < 1$ , then  $n < \kappa$  and the wavelength  $2\pi c/\omega n$  is greater than the logarithmic damping factor, i. e., the distance in which the amplitude decreases by a factor  $e^{-2\kappa}$  or 0.2%. No wave can actually develop at all under such circumstances. The field is quasistatic and its distribution in space is similar to a static one. If indeed  $\omega^2 \lambda^2$  and  $\omega \sigma \lambda$  are small numbers, the following approximations hold:

$$n = \frac{1}{2} \sigma \lambda^{3/2}, \quad \kappa = \frac{1}{\omega \lambda^{3/2}} \gg n \quad (15-8)$$

This can be seen in the simplest way by forming  $n^2 - \kappa^2$  and  $2n\kappa$  from eq. 15-8, and comparing with eq. 15-6. Since in this case  $\omega \lambda/c = \beta$ , the amplitude decreases by the factor  $e^{-\beta}$  just as in the static case.

On the other hand if  $\omega^2 \lambda^2 > 1$ , then  $n > \kappa$  according to eq. 15-7, and the wavelength is therefore smaller than the logarithmic damping factor, so a whole series of waves is produced with only gradually decreasing amplitude. If indeed  $\omega^2 \lambda^2 \gg 1$ , then the unity in the numerator of eq. 15-6 is negligible and we obtain the approximate values

$$n = 1 + \frac{(\sigma/\omega)^2}{8}, \quad \kappa = \frac{\sigma}{2\omega} \quad (15-9)$$

which no longer depend on the superconductivity constant  $\lambda$ .

But such a condition can only be realized immediately below the transition temperature where  $\lambda$  is comparatively large. As soon as  $\lambda$  attains values of the order  $10^{-31}$  sec<sup>2</sup> at somewhat lower temperatures, this condition is hardly possible any longer because, just as with the Maxwell theory, our theory cannot be regarded as valid for arbitrarily high frequencies. Let us consider the situation with mercury for which direct determinations of  $\beta$ , and therefore also of  $\lambda$ , are available (see Chap. 1 and 12). Its conductivity  $\sigma$  at room temperatures is about  $10^{17}$  sec<sup>-1</sup> in Lorentz units ( $4\pi$  times its value in esu); it is about 500 times greater just above the transition temperature:  $10^{19}$  sec<sup>-1</sup>. Therefore for  $\omega = 10^{10}$  per sec,  $\omega^2 \lambda^2 = 10^{-11}$ , and  $\omega \sigma \lambda = 10^{-2}$  (short Hertzian waves, high radio frequency), and for  $\omega = 10^{14}$  per sec,  $\omega^2 \lambda^2 = 10^{-3}$  and  $\omega \sigma \lambda = 10^2$  (infrared waves).

In the first case the ohmic current is about one hundred times smaller than the supercurrent; in the second case about one hundred times greater, according to eq. 15-2. In the first case the unity is the dominating term in the numerator of eq. 15-6; in the second case the number  $i \omega \sigma \lambda$ , so that, just as for a normal conductor,

$$n - i \kappa = (1 - i) \sqrt{\frac{\sigma}{2\omega}} \quad (15-10)$$

his indicates a complete identity between normal and superconductors for all optical processes. If only the supercurrent were to exist in the superconductor, then the superconductor would be transparent. The fact that there is no visible difference between the normal and the superconductor [chap. 1 (d)] is a decisive proof of the existence of the ohmic current.

For  $\omega = 10^{14}$  per sec and  $\sigma = 10^{10}$  per sec, eq. 15-10 gives  $n$  and  $x$  of order of magnitude between  $10^2$  and  $10^3$ .

(c) If  $\omega = 10^{10}$  per sec then according to the above figures the conditions for the validity of eq. 15-8 are satisfied. The refractive index  $n$  has the order of magnitude  $10^3$  and the extinction coefficient  $10^2$  for radio frequency waves. The reflectivity of a specimen for a wave incident perpendicularly from empty space can be calculated from the well-known optical expression

$$\frac{(n-1)^2 + x^2}{(n+1)^2 + x^2}$$

under the present conditions this expression can be simplified to read

$$\frac{1 + \left(\frac{n-1}{x}\right)^2}{1 + \left(\frac{n+1}{x}\right)^2} = 1 - \frac{4n}{x} = 1 - 2\omega^2 \sigma \lambda^4 \quad (15-11)^1$$

Consequently that fraction of the energy given by the second term is absorbed by the superconductor and amounts, according to the figures used above, about 10-8.

## CHAPTER 16

### The High-Frequency Resistance of Superconductors

(a) A direct current is distributed uniformly over the cross section of a normally conducting cylinder. Alternating current, however, is confined to a thin layer at the surface which becomes thinner with increasing frequency. The induction from the magnetic field of the alternating current protects the interior from the current. This is the "skin effect" that exists in conductors of any form. In the superconductor a tendency to the skin effect already exists even with the direct current because of the coupling between the supercurrent and the magnetic field expressed by eq. X. High frequency alternating current thus Meissner effect and the skin effect reinforce each other. The penetration depth of the field of such an alternating current is then smaller than for direct current in the super-

<sup>1</sup> See the discussion of eq. 16-18 for the meaning of the number  $\omega^2 \sigma \lambda^4$ .

conductor and smaller than for alternating current of the same frequency in a normal conductor. The skin effect eventually causes a very substantial decrease in the cross section that actually carries the current in a normal conductor and thus may cause a considerable increase of the resistance. A changing field, according to Chaps. 7 and 15, produces an average resistance in a superconductor. This resistance increases with increasing frequency not only because of the decrease of the conducting cross section, but also because of the increasing transfer of current from the supercurrent to the ohmic current in accordance with eq. 15-2. We shall describe this increase quantitatively for the cubic crystal material.

(b) First we have to determine the current density as a function of position. The telegrapher's equation of Chap. 6 for the total current density reads:

$$W(i) \equiv \Delta i - \frac{1}{c^2} \frac{\partial^2 i}{\partial t^2} - \frac{\sigma}{c^2} \frac{\partial i}{\partial t} - \frac{i}{\lambda^2 c^2} = 0$$

For periodic processes this becomes

$$\Delta i - i \frac{(\omega^2 + i\omega\sigma + \lambda^{-1})}{c^2} = 0$$

As we are confining ourselves to frequencies less than  $10^{10}$  per sec, the first term in the brackets is small compared with the second term when  $\sigma = 10^{10}$  per sec (see Chap. 15). We therefore neglect this term and write

$$\Delta i - k^2 i = 0$$

for superconductors where

$$k = \frac{(1 + i\omega\sigma\lambda)^{1/2}}{c\sqrt{\lambda}} \quad (16-1)^1$$

As the neglected term arises from the term  $\partial E/\partial t$  in the fundamental equation II, it means we are neglecting the displacement current as compared with the conduction current. We complete the definition of  $k$  by choosing both its roots to be positive, i. e., both the real and the imaginary part of  $k$  shall be positive.

Going to the limit  $\lambda \rightarrow \infty$  leads to the normal conductor, because in this limit the last term of  $W(i)$  vanishes and instead of eq. 16-1 we have the differential equation

$$\Delta i - k_n^2 i = 0, \quad k_n = \frac{\sqrt{i\omega\sigma}}{c} \quad (\text{normal conductor}) \quad (16-2)$$

In both cases the boundary conditions are:  $\text{div } i = 0$ ,  $i$  is finite and continuous throughout the interior; and, because we are discussing quasi-stationary currents,  $i_n = 0$  at all surfaces; and finally integration of  $i$

<sup>1</sup> The following relation exists between  $k$  and the refractive index and extinction coefficient:

$$k = i\omega \frac{(n - ix)}{c}$$

ver any cross section yields the total current strength  $I e^{i\omega t}$ . We treat as a real quantity.

We obtain the magnetic field from the current density by the fundamental equation II<sub>2</sub> which, neglecting the displacement current, reads:

$$\text{curl } \mathbf{H} = \frac{1}{c} \quad (16-3)$$

the external space we have the additional requirement that  $\mathbf{H}$  is the negative gradient of a potential obeying the equation  $\Delta \varphi = 0$ . Besides requiring that  $\mathbf{H}$  be divergence free, the boundary conditions require also that  $\mathbf{H}$  be finite and continuous at the surface of the conductor, and vanish sufficiently rapidly at infinity. The calculations are carried out in the same way for both the superconductor and the normal conductor except that the first case one has to use the  $k_n$  of eq. 16-1 and in the other the  $k_n$  eq. 16-2.

We can also derive the electric field from the current density. For the normal conductor we use the fundamental equation VII<sub>2</sub>,

$$\mathbf{E} = \frac{1}{\sigma} \quad (\text{normal conductor})$$

file for the superconductor we use eq. 15-3,

$$\mathbf{E} = \frac{i\omega\lambda}{(1+i\omega\sigma\lambda)} \quad (\text{superconductor})$$

can therefore derive the field strength for the superconductor from it of the normal conductor by multiplying the latter by the factor

$$\frac{(1+i\omega\sigma\lambda)}{i\omega\sigma\lambda} \quad (16-4)$$

the last step consists of determining the Poynting energy current vector  $\mathbf{E} \times \mathbf{H}$ . The divergence of the time average of this vector gives the heat per unit volume and unit time, and the integral  $\oint [\mathbf{E} \times \mathbf{H}] \cdot d\mathbf{a}$  therefore the Joule heat developed in the enclosed volume per unit time. In the complex solutions for  $\mathbf{E}$  and  $\mathbf{H}$  obtained in the manner just described, we calculate the time average of the Joule heat as the real part of  $[\mathbf{E} \times \mathbf{H}^*]$ , where  $\mathbf{H}^*$  is the complex conjugate to  $\mathbf{H}$ .

If one has the complex representations for two field quantities  $A$  and  $B$ :

$$A = A_0 e^{i\omega t} = |A_0| e^{i(\omega t - \varphi)}, \quad B = B_0 e^{i\omega t} = |B_0| e^{i(\omega t - \psi)}$$

each represent two real quantities, one pair of which is

$$A = |A_0| \cos(\omega t - \varphi), \quad B = |B_0| \cos(\omega t - \psi)$$

time average of the product of the two quantities is then

$$\frac{1}{2} |A_0| |B_0| \cos(\varphi - \psi)$$

result can be obtained most simply from the complex representation as

$$\frac{1}{2} \text{Real Part of } (A B^*)$$

Having calculated  $\frac{1}{2} c [\mathbf{E} \times \mathbf{H}^*]$  for the normal conductor, we obtain its value for the superconductor by substituting  $k_n$  for  $k_n$  and multiplying by the factor 16-4. From the real part of this we derive the Joule heat  $Q$  and the resistance

$$R = \frac{Q}{I^2} \quad (16-5)$$

As the factor 16-4 becomes unity, and  $k_n \rightarrow k_n$  when  $\lambda$  approaches infinity, the resistance of the superconductor goes over continuously into that of the normal conductor at the transition temperature provided that the conductivity  $\sigma$  is not discontinuous there.

The simplest solutions of the differential equations 16-1 and 16-2, corresponding to the plane waves already discussed in Chap. 15, are

$$\mathbf{H} = \mathbf{H}_0 e^{-k_n z} \quad \text{or} \quad \mathbf{H} = \mathbf{H}_0 e^{-k_n z}$$

Evidently the real part of  $k_n$  or of  $k_n$ , respectively, determines the decrease of amplitude with increasing  $z$ . Separating the real and imaginary parts of  $k_n$  and  $k_n$ ,

$$k_n = \frac{1}{c\sqrt{2\lambda}} \{ [1 + \sqrt{1 + (\omega\sigma\lambda)^2}]^{1/4} + i [-1 + \sqrt{1 + (\omega\sigma\lambda)^2}]^{1/4} \} \quad (16-6)$$

$$k_n = \sqrt{\frac{1}{2} \frac{\omega\sigma}{c}} \frac{(1+i)}{c} \quad (16-7)$$

The real part of  $k_n$  is thus greater than that of  $k_n$ , or waves in the superconductor decay more rapidly toward the interior than they do in the normal conductor, other things being equal, as already observed in section (a).

(c) Using the method described above we calculate the a-c resistance of a circular cylinder of radius  $R$  carrying a current  $I e^{i\omega t}$ , first for a normal conductor. We use the same cylindrical coordinates as in Chap. 8. As the differential equation 16-2 differs from  $\Delta u - \beta^2 u = 0$  only in the notation used for the constants, we can take over eq. 8-9 for the current by replacing  $\beta$  by  $k_n$  and  $I$  by  $I e^{i\omega t}$ .

$$I_r = 0, \quad I_\theta = 0, \quad I_z = \frac{i k_n I}{2\pi R} e^{i\omega t} \frac{J_0(\epsilon k_n r)}{J_1(\epsilon k_n R)} \quad (16-8)$$

Taking over eq. 8-11 in the same way satisfies eq. 16-3:

$$\mathbf{H}_r = 0, \quad \mathbf{H}_\theta = \frac{I}{2\pi c R} e^{i\omega t} \frac{J_1(\epsilon k_n r)}{J_1(\epsilon k_n R)}, \quad \mathbf{H}_z = 0 \quad (16-9)$$

For thin cylinders ( $k_n R \ll 1$ ) to a first approximation  $J_0(x) = 1$  and  $J_1(x) = \frac{1}{2}x$ ; compare the series 8-6. We therefore conclude, as in Chap. 8, that the current is uniformly distributed over the cross section in this case. For thick cylinders ( $k_n R \gg 1$ ) we have approximately:

$$J_0(\epsilon k_n r) = (2\pi \epsilon k_n r)^{-1/2} \left( 1 + \frac{1}{8\epsilon k_n r} \right) \exp \left( \epsilon k_n r + \frac{1}{4} \pi i \right) \\ J_1(\epsilon k_n r) = (2\pi \epsilon k_n r)^{-1/2} \left( 1 - \frac{1}{8\epsilon k_n r} \right) \exp \left( \epsilon k_n r + \frac{3}{4} \pi i \right) \quad (16-10)^3$$

<sup>3</sup> It is essential here that the real part of  $k_n$  be positive.

It follows that  $\mathbf{I}$  and  $\mathbf{H}$  decay exponentially with decreasing  $r$ . There is a protective layer of thickness  $(\text{Re } k_n)^{-1}$  in this case and the skin effect is pronounced.

The Poynting energy flow vector has only one component, an  $r$  component with magnitude  $c \mathbf{E} \cdot \mathbf{H}_\theta = -(c/\sigma) \mathbf{I}_r \cdot \mathbf{H}_\theta$ . The mean rate at which energy enters unit length of the cylinder is therefore

$$Q = 2\pi R \frac{c}{2\sigma} \text{Re}(\mathbf{I}_r \cdot \mathbf{H}_\theta^*)_{r=R} \quad (16-11)$$

Let  $Z$  be defined in such a way that

$$Q = I^2 \text{Re}(Z) \quad (16-12)$$

so that by eq. 16-5 the resistance per unit length is

$$W = \text{Re}(Z) \quad (16-13)$$

However, from eqs. 16-8 and 16-9

$$Z = \frac{1}{\sigma \pi R^2} \left( \frac{1}{2} \epsilon k_n R \right) \frac{I_0(\epsilon k_n R)}{I_1(\epsilon k_n R)} \quad (\text{normal conductor}) \quad (16-14)$$

the first fraction is the d-c resistance of the normal conductor. For thin cylinders the other fractions reduce to unity according to eq. 8-6.

This well-known result for the a-c resistance of the normal conductor holds for the superconductor if we write  $k$  instead of  $k_n$  and multiply with the factor 16-4. The resistance then becomes the real part of

$$Z = \frac{1}{\sigma \pi R^2} \left[ \frac{\omega \sigma \lambda}{(1 + \omega \sigma \lambda)} \right] \left( \frac{1}{2} \epsilon k R \right) \frac{I_0(\epsilon k R)}{I_1(\epsilon k R)} \quad (\text{superconductor}) \quad (16-15)$$

(d) We limit the discussion of this equation to the case of a thick cylinder,  $k|R \gg 1$ . From eq. 16-10 it follows for this case that

$$\frac{I_0(\epsilon k R)}{I_1(\epsilon k R)} = -\epsilon \left( 1 + \frac{1}{2kR} \right) \quad (16-16)$$

Noticing eq. 16-1 we see that this reduces eq. 16-14 to

$$Z = \frac{1}{2\pi c R} \left( \frac{\omega \lambda}{1 + \omega \sigma \lambda} \right) \left[ 1 + \frac{1}{2} \epsilon \sqrt{\lambda} \frac{(1 + \omega \sigma \lambda)^{-1/2}}{R} \right] \quad (16-17)$$

assume at first that  $\omega \sigma \lambda \ll 1$ , which is surely justified when  $\omega \leq 10^{10}$  r sec and  $\lambda = 10^{-31}$  sec<sup>2</sup> (see Chap. 15). Developing the denominator eq. 16-16 in series we then find

$$Z = \frac{\omega^2 \sigma \lambda^2}{4\pi c R} + \frac{\omega^2 \sigma \lambda^2}{4\pi R^2} + \epsilon \left( \frac{\omega \lambda^{1/2}}{2\pi c R} + \frac{\omega \lambda}{4\pi R^2} \right) \quad (16-18)$$

Inside the real part of eq. 16-17, the resistance  $W$ . Its value is

$$W = \frac{\omega^2 \sigma \lambda^2}{4\pi c R} = \frac{(\omega \sigma \lambda)^2}{4\pi \sigma c R \sqrt{\lambda}} \quad (16-19)$$

except for an additional term only  $c/\lambda \div R$  compared with the first term  $c/\lambda$  is the penetration depth).

The resistance turns out to be proportional to  $(\omega \sigma \lambda)^2$  because the number  $\omega \sigma \lambda$  is a measure of the extent to which the ohmic current  $\mathbf{i}$  participates in the transport of electricity, whereas the Joule heat is proportional to the square of  $\mathbf{i}$ . In the denominator of eq. 16-18 there is the product of the cylinder's circumference,  $2\pi R$ , and the penetration depth  $c/\lambda$ , and this is an approximate measure of the area that carries the current. Multiplying this is the conductivity  $\sigma$ , because it is this product of cross-sectional area and conductivity that matters. We may take  $c/\lambda$  rather than the reciprocal of the real part of  $k$  to be the penetration depth because the supercurrent far outweighs the ohmic current in the present approximation.

Equation 16-18 can be used for all temperatures that are at least some tenths of a degree below the transition temperature, for  $\lambda$  then has the assumed order of magnitude,  $10^{-31}$  sec<sup>2</sup>. With increasing temperature  $\lambda$  increases and so does the resistance. However, some tenths of a degree below the transition temperature,  $\lambda$  becomes so great that the equation fails.

To discuss the temperature dependency of the resistance in general we introduce the auxiliary quantity  $\theta$  defined by

$$\omega \sigma \lambda = \tan \theta \quad 0 < \theta \leq \frac{1}{2}\pi \quad (16-20)$$

Neglecting the small second term inside the bracket in eq. 16-16 we get the transformation

$$2\pi c R Z = \epsilon \omega \sqrt{\lambda} \cos \theta e^{-1/2\theta}$$

The real part of this is therefore

$$2\pi c R W = \int_0^{\omega \sqrt{\lambda} \cos \theta} \frac{1}{\sigma} \sqrt{\omega \sigma \lambda \cos \theta} \sin \frac{1}{2}\theta = \int_0^{\omega \sqrt{\lambda} \cos \theta} \frac{1}{\sigma} \sqrt{\sin \theta} \sin \frac{1}{2}\theta$$

At the transition temperature  $\lambda = \infty$  and therefore  $\theta = \frac{1}{2}\pi$ . As the conductivity has perhaps a different value  $\sigma_c$  at the transition temperature than at lower temperatures, we have to put

$$2\pi c R W_c = \int_0^{\omega} \frac{\omega}{2\sigma_c} \quad (16-21)$$

Dividing eq. 16-20 into the previous equation yields

$$\frac{1}{\sigma} \frac{W}{W_c} = \sqrt{2} \sin \theta \sin \frac{1}{2}\theta \quad (16-22)$$

From the way it was derived, eq. 16-20 evidently gives the resistance of a normal conductor having conductivity  $\sigma_c$ , assuming a pronounced skin effect:  $\text{Re}(k_n R) \gg 1$ . This is easily confirmed from eqs. 16-3 and 16-15. Therefore eq. 16-21 again shows that there is a continuous transition from the high-frequency resistance of the normal conductor to that of the superconductor.

(e) All quantities depending on the geometry of the superconductor have disappeared from eq. 16-21, and in fact this equation holds for other forms than the straight circular cylinder.

To see this let us consider a normal conductor having some elongated form to the ends of which the current leads are attached, at a distance  $L$  apart. It could, for example, be a wire wound in the form of a coil. Its d-c resistance would be  $L/\sigma A$ , where  $A$  is the mean cross section. However, for alternating current with pronounced skin effect, the current does not fill the whole cross section, but only a thin superficial layer the thickness of which is given by  $(\text{Re } k_n)^{-1}$ . Let the cross section of this surface layer have a mean linear dimension  $S$  normal to its thickness. Then the resistance becomes  $W = L(\text{Re } k_n)/\sigma S$ .

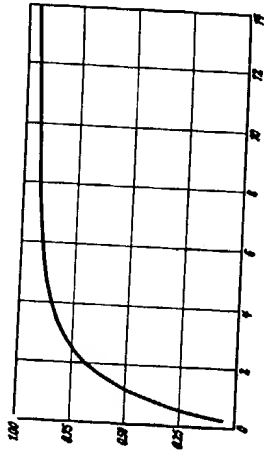


Fig. 16-1. Curve of  $\frac{1}{2} \sin \theta \sin \frac{1}{2} \theta$  against  $\tan \theta$ .

As the example of the cylinder shows, the calculation leads initially to a complex quantity  $Z$  the real part of which is the resistance  $W$ . The imaginary parts of  $k_n$  do not appear explicitly. In fact the eq. 16-13 has this form if we remember that it refers to  $L = 1$ , and if, in accordance with eq. 16-15 we put the ratio of the Bessel functions equal to 1. Going over to the superconductor, which requires the replacement  $k_n$  by  $k$  and the multiplication by the factor 16-4 we obtain

$$Z = \frac{Lk}{S\sigma(1 + i\omega\sigma\lambda)}$$

again applying eq. 16-15 we confirm that the factor  $(L/S)$  equals the factor  $(1/2\pi R)$  in eq. 16-14. This means, however, that the transformation  $cS W/L$ , thus again leading to eq. 16-21.<sup>4</sup> We repeat: In all these implies it is important that the skin effect should already be pronounced

<sup>4</sup>A. Sommerfeld [Ann. Physik (4) 24, 609 (1907)] has calculated the correction q. 16-13 needed for a normally conducting wire wound in the form of a coil. For pronounced skin effect, it consists of a real factor depending only on the spacing between successive windings of the coil and the radius of the wire. The same factor has to imply  $W = \text{Re } (Z)$ , it can be taken over unchanged for the superconducting wire so cancels in eq. 16-21 when forming the ratio  $W/W_s$ .

in the normal conductor. It is only if the smallest possible value of  $|k_n|$ , namely  $|k_n|$ , satisfies the condition  $|k|/R \gg 1$  that eq. 16-21 can be used for the cylinder.

(f) Let us reduce the temperature  $T$  starting from the transition temperature  $T_s$ . According to eq. 16-19  $\theta$  then decreases monotonically with  $\lambda$ , and the same is true of the function  $\frac{1}{2} \sin \theta \sin \frac{1}{2} \theta$  (Fig. 16-1). If finally the number  $\omega\sigma\lambda$  becomes small compared with unity, owing to the decrease of  $\lambda$ , then also  $\theta \ll 1$  and  $\frac{1}{2} \sin \theta \sin \frac{1}{2} \theta$  has the value  $(\omega\sigma\lambda)^{1/2}$ . Therefore, according to eq. 16-21, we have

$$W = W_s \sqrt{\frac{\sigma_s}{2\omega}} \omega^2 \sigma \lambda^{1/2},$$

in agreement with eq. 16-17.  $W$  should decrease monotonically between this value and  $W_s$  provided the conductivity  $\sigma$  remains constant. However, the curves published by McLennan and co-workers [Chap. 1 (c)] for the resistance of tantalum as a function of temperature for frequency  $\omega = 2\pi \cdot 1.14 \times 10^7$  per sec, i. e., the upper curve of Fig. 16-2 shows an initial maximum at which  $W$  is 4% higher than  $W_s$ , and only after this does the expected decrease appear. If this maximum is real,<sup>5</sup> it can only be interpreted as due to the conductivity  $\sigma$  starting to decrease at the transition temperature; according to eq. 16-21 the product  $\sqrt{\sigma} W$  must decrease immediately below the transition temperature.

It is evidently impossible to determine both  $\sigma$  and  $\lambda$  as functions of  $T$  from a single empirical curve. But by using the empirical curve for  $W$  we can try to find a plausible form for  $\sigma$  as a function of  $T$  such that one derives a curve for  $\lambda$  that has a steep decline just below  $T_s$ , similar to that found in the experiments of Appleyard and Shoenberg with mercury [Chap. 1 (c)]. If  $W$  and  $\sigma$  are given for a certain  $T$ , then eq. 16-21 ascribes to this  $T$  a certain  $\theta$  value, and eq. 16-19 a certain  $\lambda$  to this  $\theta$ . We try the form

$$\frac{\sigma}{\sigma_s} = 0.6 + 0.4 \times e^{-5(T_s - T)} \quad (16-22)$$

<sup>5</sup>Recent work on resonant cavities instead of wires failed to show this maximum. J. C. Slater, E. Maxwell, P. Marcus, Phys. Rev. 76, 1332, (1949). B. Pippard, Proc. Roy. Soc. (London), 191, 370, 385, 399 (1947). 208, 195, 210, (1950).

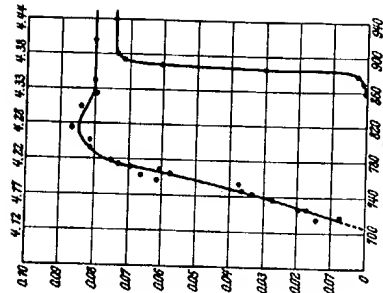
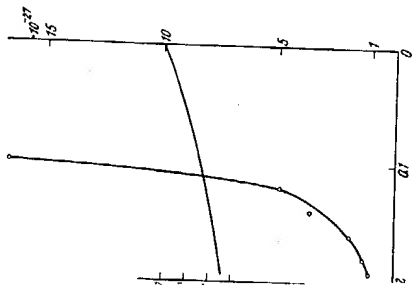


Fig. 16-2. Resistance of tantalum near the transition temperature.

according to which  $\sigma$  decreases to  $0.6\sigma_0$  within one degree and then remains constant. The empirical values of  $\sigma_0$  differ. The finding of McLennan and his co-workers that the d-c resistance of tantalum at  $T_c$  is  $0.07$  of the resistance at  $0^\circ\text{C}$  leads to  $\sigma_0 = 1.30 \times 10^{10}$  per sec in Lorentz units, and we shall use this value. If it is wrong by a factor  $\alpha$ , then all  $\sigma$  values have to be multiplied by  $\alpha$ , and all  $\lambda$  values by  $1/\alpha$ , which does not change the form of the  $\lambda$  curve. The result of this calculation is shown in Fig. 16-3. The curve has indeed the expected form. Figure 11-3 gives the measurements of  $\lambda$  for mercury for comparison.



16-3. Superconductivity constant and relative conductivity of aluminum as a function of temperature. Abscissa: temperature difference  $-T$ , increasing toward the left. Ordinate: the steeper curve is the superconductivity constant in sec $^{-1}$  by the scale on the right-hand side; the flatter curve is  $(\sigma/\sigma_0)$  given by the left-hand scale according to the assumption 16-22.

(g) H. London measured the resistance of superconducting tin at frequencies of about  $10^{10}$  cycles per second by producing eddy currents in ellipsoidal specimen and calculating the heat produced by measuring rate of evaporation of the helium bath. He also found that the high frequency resistance of the normal conductor passes continuously into that of the superconductor at the transition temperature, and that there is a steep drop when we further decrease the temperature.

The considerations of this chapter become meaningless — as does the well theory itself — if the mean free path of the electrons becomes

comparable with or greater than the penetration depth. Deviations of this kind were first observed by Pippard<sup>6</sup> and by Slater and co-workers.<sup>7</sup> A theoretical treatment of this problem has been given by Reuter and Sondheimer<sup>8</sup> and Slater *et al.*<sup>9</sup>

## CHAPTER 17

### Thermodynamics of the Transition between Normal and Superconducting Phases

(a) It was the Meissner effect that led to the idea that the superconducting and the normally conducting states are different phases of the same material in the sense that diamond and graphite are different phases of carbon. Earlier, when it was supposed that any arbitrary magnetic field could be "frozen in" within the interior of a superconductor (see Chap. 1) one had to presume an infinity of different superconducting states, and this excluded the phase idea. We know now, however, that the interior of a sufficiently thick superconductor in a stationary state is field free, protected by the thin surface layer, regardless of its history. Even if the metal is too thin to form this protective layer, the field in its interior is uniquely determined by the conditions imposed by the magnetic field in its neighborhood at the moment of interest, and independent of its previous history, always supposing this field to be stationary and changes of state as quasi-stationary just as we do in all thermodynamic arguments.

However, the superconducting and normally conducting phases are much more alike than are diamond and graphite. At all temperatures they have the same lattice structure, not only with regard to symmetry characteristics, but also the same lattice constants. Shape and volume are completely preserved during the transition. This point is essential to the following application of thermodynamics. It would not be if the transition between the two phases were effected by means of an intermediate vapor phase, a certain amount of one phase evaporating, the same amount condensing into the other solid phase. But in the present case one solid phase changes directly into the other, which is in contact with it; only the identity of the two lattices prevents the system from splitting into more or less minute fractions (being of the form single crystal  $\rightarrow$  polycrystal which would naturally exclude any reversibility).

<sup>6</sup> B. Pippard, *Proc. Roy. Soc. (London)*, 191, 370, 385, 399 (1947).

<sup>7</sup> J. C. Slater, E. Maxwell, P. Marcus, *Phys. Rev.* 76, 1532, (1949).

<sup>8</sup> G. E. H. Reuter and E. H. Sondheimer, *Proc. Roy. Soc. (London)*, 195 A, 336 (1948).

Incidentally Keesom and Kok<sup>1</sup> (for tellurium) and van Laer and Keesom<sup>2</sup> (for tin) have experimentally compared the heats of reaction during the transition both from the superconducting to the normal state and during the reverse transition and have found them equal, as required for reversibility.

A further assumption, supported indeed by the arguments of Chap. 5, is that the free energy of the magnetic field, including the superconduction energy is added to the free energy of the specimen, and so there is no free energy of interaction. This permits the following concept. The field is a "machine" exerting the forces on the surface of the superconductor that are given by the London stress system as discussed in Chap. 13. These forces perform work in so far as the surface is displaced, and this work serves to change the free energy of the material during isothermal displacements. The free energy of the field does not enter such a calculation, the internal changes of the "machine" being irrelevant for the energy balance in the specimen.

As shown in Chaps. 13 and 14 the force due to the field at a point where no current crosses the surface — the current lines being parallel to the surface — is a stress of amount  $\frac{1}{2}(\mathbf{i} \cdot \mathbf{G})$  directed toward the interior of the superconductor. We shall calculate this example first.

(b) To do this we write  $f_s$  and  $f_N$  for the free energies ( $f = e - Ts$ ) per mol of the superconductor and normal conductor respectively and  $V$  for the mol volume common to both phases, with  $d\sigma$  a surface element of the superconductor and  $\delta n$  a virtual displacement of this element in the direction of its normal.  $\delta n$  is taken positive for displacements toward the interior of the superconductor as in Chap. 14 (/). It is necessarily positive wherever the superconductor borders upon empty space or a chemically different specimen, but  $\delta n$  can be negative if the superconductor joins on to a chemically identical normal conductor. For positive  $\delta n$ ,  $d\sigma \cdot \delta n/V$  mols of the superconductor change into normal conductor; the tension of the London stresses performs work  $\frac{1}{2}(\mathbf{i} \cdot \mathbf{G}) \delta n \cdot d\sigma$  (Chaps. 13 and 14) while the free energy of the material increases by  $(f_N - f_s) d\sigma \cdot \delta n/V$ . For negative  $\delta n$  the corresponding number of mols of normal conductor change into superconductor; the work done by the forces becomes negative. Naturally it is impossible for a single element alone to be displaced as the continuity of the boundary must be preserved, but an arbitrary infinitesimal displacement  $\delta n$  can be ascribed to any element  $d\sigma$  of the surface. The total number of mols going over from one phase into the other is  $\int \delta n \cdot d\sigma/V$  and the work done by the forces is

$$\delta A = \int \frac{1}{2}(\mathbf{i} \cdot \mathbf{G}) \delta n \cdot d\sigma \quad (17-1)$$

The corresponding change in free energy is

<sup>1</sup>W. H. Keesom and J. A. Kok, *Physica*, **1**, 503 (1934).

<sup>2</sup>P. H. van Laer and W. H. Keesom, *Physica*, **5**, 993 (1938).

$$\delta F = \left[ \frac{(f_N - f_s)}{V} \right] \int \delta n \cdot d\sigma \quad (17-2)$$

From the two principal laws of thermodynamics one concludes that for a spontaneous isothermal transition  $\delta A > \delta F$ . The necessary condition that a transition shall not occur is therefore

$$\delta A \leq \delta F$$

Applied to the displacement of the boundary this gives

$$\frac{1}{2} \int (\mathbf{i} \cdot \mathbf{G}) \delta n \cdot d\sigma \leq \left[ \frac{(f_N - f_s)}{V} \right] \int \delta n \cdot d\sigma$$

Since  $\delta n$  can be either positive or negative, the inequality must reduce to equality: because if for some choice of  $\delta n$  the right-hand side were greater than the left side, it would be smaller for the opposite choice of  $\delta n$ . Furthermore, as  $\delta n$  is an arbitrary function of position on the surface, equilibrium must exist at every point:

$$\frac{1}{2}(\mathbf{i} \cdot \mathbf{G}) = \frac{(f_N - f_s)}{V} \quad (17-3)$$

This is the equilibrium condition for the boundary between super- and normal conductor. If  $\delta n$  is necessarily positive at the surface of a superconductor bordering empty space or a chemically different specimen the condition for conservation of superconductivity is

$$\frac{1}{2}(\mathbf{i} \cdot \mathbf{G}) \leq \frac{(f_N - f_s)}{V} \quad (17-4)$$

In this form both conditions are valid for "thick" superconductors with fully developed protective layers, as well as for the "thin" superconductors in which the magnetic field penetrates more or less completely. Since experiments almost always deal with "thick" superconductors these conditions are usually expressed instead in terms of the magnetic field at the surface, derived from the supercurrent there by the eq. 7-37 valid for "thick" superconductors. We define a field strength  $H_c$  by

$$\frac{1}{2} H_c^2 = \frac{(f_N - f_s)}{V} \quad (17-5)$$

The condition 17-3 for the boundary between super- and normal conductor reads

$$H = H_c \quad (17-6)$$

and the condition 17-4 for a boundary surface adjacent to empty space or a chemically different material:

$$H \leq H_c \quad (17-7)$$

This justifies our considering  $H_c$  defined by eq. 17-5 as a critical field. It is a necessary consequence of this theory that if  $H$  exceeds this value at any point of the free surface of a "thick" superconductor its superconductivity is destroyed.

If the magnetic field gives rise only to permanent magnetism and annular currents in superconductors, then according to Chap. 14 (e) the work  $\delta A$  performed by the field is equal to the decrease  $(-\delta U)$  of the free energy of the field. Equation 17-3 states that in this case the sum of the free energy of the field and the specimen is conserved during the reversible phase transition. This statement however does not hold if ohmic currents are also produced, or if only ohmic currents are produced by the field. In this case the system (field plus specimen) is not a closed system. Additional electrostatic forces are required to fulfill the condition that the ohmic currents remain constant. If we wish to use the theorem of constant free energy we have to be quite clear about how the field is produced.

(c) These conclusions can also be derived for a "thick" superconductor from the volume forces exerted according to Chap. 13 by the Maxwell stresses,  $[\mathbf{i} \times \mathbf{H}]/c$ , on the supercurrent mechanism of the London theory. These forces are distributed over the thickness of the protecting layer. However, in the "thick" superconductor this protecting layer undergoes the virtual displacement  $\delta n$  as a whole without alteration of field or current distribution, so that we can calculate the work done by these forces per unit surface as the product of the resultant force per unit area times  $\delta n$ . As there is no field inside the layer, the resultant force is the pressure  $\frac{1}{2} H^2$  of the lines of force on the outside, by Chap. 13. In this way we get the equilibrium condition

$$\delta A = \frac{1}{2} \int H^2 \delta n \cdot d\sigma \leq \left[ \frac{(f_N - f_S)}{V} \right] \int \delta n \cdot d\sigma$$

and from this, the eqs. 17-6 and 17-7. This conclusion cannot be assumed so easily for thin superconductors where the field and current distribution change in a complicated fashion with a displacement  $\delta n$  of the surface.

This derivation has the advantage of being based more directly on the Meissner effect, i. e., the existence of the protective layer, than was the first derivation; but the latter is more general and can be used also for thin specimens.

(d) The free energies  $f_N$  and  $f_S$  are functions of the temperature  $T$ . We neglect their dependence on pressure or elastic stress because most experiments have been performed on strain-free specimens at one atmosphere which is effectively zero pressure. According to eq. 17-8 the critical value  $H_c$  is also a function of  $T$ . From thermodynamics we have<sup>3</sup>

$$s = -\frac{d}{dT} \quad (17-8)$$

for the entropy per mol,  $s$ , and we obtain eq. 17-5 by neglecting the extremely small changes in volume  $V$  at these temperatures in accordance with Nernst's theorem, thus:

$$s_N - s_S = -\frac{1}{2} V \frac{d(H_c^2)}{dT} = -V H_c \frac{dH_c}{dT} \quad (17-9)$$

<sup>3</sup> The specific heat does not depend on magnetic field (see discussion of Fig. 17-2) so we may write  $dH/dT$  instead of  $(\partial H/\partial T)_H$ .

This is the increase in entropy associated with the transfer of one mol from the superconducting to the normal state. Multiplying by  $T$  we get the amount of heat that has to be supplied with this transition:

$$Q = -\frac{1}{2} V T \frac{d(H_c^2)}{dT} = -V T H_c \frac{dH_c}{dT} \quad (17-10)$$

Further we have the following expression for the specific heat per mol at constant pressure:

$$c = T \frac{ds}{dT} = -T \frac{d^2 Q}{dT^2} \quad (17-11)$$

So from eq. 17-9 we have

$$c_N - c_S = -\frac{1}{2} V T \frac{d^2(H_c^2)}{dT^2} = -V T \left[ \left( \frac{dH_c}{dT} \right)^2 + H_c \frac{d^2 H_c}{dT^2} \right] \quad (17-12)$$

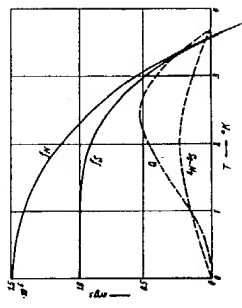


Fig. 17-1. Thermodynamic functions for tin below the transition temperature  $f_N$  and  $f_S$  are the free energies per mol in the normal and superconducting states. The curves split at the transition temperature  $3.7^\circ \text{K}$ . Only the difference  $f_N - f_S$  has physical meaning. The upper dotted curve gives the heat  $Q$  in ergs per mol to be supplied during the transition of the superconductor into the normally conducting state. The lower dotted curve is the entropy difference  $s_N - s_S$  in ergs per mol degree. The figures used come from eqs. 17-16 and 17-17:

$$\begin{aligned} f_N &= -2.54 \times 10^5 \text{ T}^4 - 8.40 \times 10^3 \text{ T}^2 + 1.50 \times 10^6 \text{ erg/mol} \\ f_S &= -5.92 \times 10^5 \text{ T}^4 + 1.00 \times 10^6 \text{ erg/mol} \\ s_N - s_S &= -1.35 \times 10^5 \text{ T}^3 + 1.68 \times 10^4 \text{ T erg/mol deg} \\ Q &= -1.35 \times 10^5 \text{ T}^4 + 1.68 \times 10^4 \text{ T}^2 \text{ erg/mol} \end{aligned}$$

(e) These relations were first derived by Rutgers<sup>4</sup> and by Casimir and Gorter.<sup>5,6</sup> We shall discuss them now in the light of the free energy curves,  $f_N$  and  $f_S$  as functions of  $T$ , represented in Fig. 17-1. The slopes or tangents

<sup>4</sup> A. J. Rutgers, *Physica*, 1, 1055 (1934); 3, 999 (1936). See also P. Ehrenfest, *Proc. Roy. Acad. (Amsterdam)*, 36, 163 (1933).

<sup>5</sup> H. B. G. Casimir and C. J. Gorter, *Physica*, 1, 300 (1934).

<sup>6</sup> A formulation also valid for thin superconductors was given by Max von Laue, see Chap. 1, footnote 7, and Chap. 3, footnote 2 (f).



give the corresponding entropy, by eq. 17-8.  $H_c$  is zero at the transition temperature  $T_s$ , by definition, therefore  $f_N = f_s$  there according to eq. 17-5, and the two curves coincide. Experiment shows that  $dH_c/dT$  is finite at  $T_s$ , so that by eq. 17-9 the two curves have a common tangent there. But by eq. 17-12 the curves differ in their second derivatives, i. e., curvature. For  $T < T_s$  we always have  $f_N > f_s$  according to eq. 17-5.

We cannot produce the curve of  $f_s$  above  $T_s$  because the superconductor does not exist there, not even as a phase that is unstable with respect to the normal conductor. We arrive at this conclusion first from the fact that the supercurrent constant becomes infinite at  $T_s$ , so that no value can be ascribed to  $\lambda$  above  $T_s$ . Secondly, from the fact that when  $f_N - f_s$  is developed in a power series in  $T - T_s$ , it must start at the square term, so that the common point of the two curves would be a stationary point;  $f_N$  would then be greater than  $f_s$  above  $T_s$ , also, which is inconsistent with the whole concept of phase transitions. Approaching the transition from above, the free energy curve divides at  $T_s$  in such a way that the two branches originating at  $T_s$  have the same initial tangent.

Experience shows that  $H_c$  increases monotonically with decreasing temperature. According to eq. 17-5 the same must be true of  $(f_N - f_s)$ . At  $T = 0$ ,  $s_N - s_N$  must vanish by the Nernst theorem. Therefore by eq. 17-9 it follows that  $(dH_c/dT)_{T=0} = 0$ . The parabola drawn in Fig. 1-4 for  $H_c$  satisfies this condition and also the condition that  $dH_c/dT$  remains finite at  $T_s$ , without however being fixed by these conditions. On the other hand  $dH_c/dT < 0$  and therefore by eq. 17-10  $Q > 0$ : *The transition from the superconducting to the normally conducting state requires heat: the converse process liberates heat.*  $Q = 0$  only at the absolute zero where also the factor  $dH_c/dT$  in eq. 17-10 vanishes as well as  $T$ , and at the transition temperature  $T_s$  where the factor  $H_c$  vanishes. Between these temperatures  $Q$  has at least one maximum. If the  $H_c$ -temperature curve is exactly parabolic as in Fig. 1-4 the only maximum is at  $T = T_s/\sqrt{2} = 0.707 T_s$ .

From the finite value of  $dH_c/dT$  at  $T_s$  we conclude by eq. 17-12 that  $dH_c/dT = 0$  and  $d^2H_c/dT^2$  is still small,  $c_N - c_s$  must be positive if  $d^2H_c/dT^2$  is everywhere negative as in Fig. 1-4. In between there must be an intersection of the curves of  $c_N$  and  $c_s$  as functions of  $T$ . The entropy difference  $s_N - s_s$  has a maximum at this point, by eq. 17-11. If the  $H_c - T$  curve were exactly parabolic, this intersection would occur at  $T = T_s/\sqrt{3} = 0.577 T_s$ . At  $T = 0$  both  $c_N$  and  $c_s$  are zero by the Nernst theorem.

In these calculations current density  $i$  and field strength  $H$  were expressed in Lorentz units. Transforming to electrostatic units  $H_c^2$  has to be multiplied by the factor  $1/4\pi$ , according to eq. 3-10. Equations 17-5, 17-10, and 17-12 expressed in electrostatic units read:

$$\frac{V H_c^2}{8\pi} = f_N - f_s \quad (17-13)$$

$$Q = \left( \frac{V T}{8\pi} \right) \frac{dH_c^2}{dT} \quad (17-14)$$

$$c_N - c_s = -\frac{1}{8\pi} V T \frac{d^2(H_c^2)}{dT^2} \quad (17-15)$$

According to eqs. 3-10 and 3-11 the general conditions 17-3 and 17-4 retain their form in the electrostatic system.

We are now in a position to derive from eq. 17-12 an equation that has often been used to check the theory against experimental evidence. By partial integration we have

$$-\int_{T_s}^{T_s} (c_N - c_s) dT = \frac{1}{2} V \int_{T_s}^{T_s} T \frac{d^2(H_c^2)}{dT^2} dT = \frac{1}{2} V \left\{ T \frac{d(H_c^2)}{dT} \right\}_{T_s}^{T_s} - \int_{T_s}^{T_s} \frac{d(H_c^2)}{dT} dT$$

At  $T_s$ ,  $H_c = 0$  and  $d(H_c^2)/dT = 0$ . Using these expressions and eq. 17-10 to transform the right-hand side we obtain

$$-Q = \frac{1}{2} V H_c^2 + \int_{T_s}^{T_s} (c_N - c_s) dT \quad (17-16)$$

This equation expresses the energy principle for the following cycle: Consider one mol of substance:

1. Cool the superconducting phase from the transition temperature  $T_s$  to  $T$ . To effect this we have to supply the (negative) amount of heat  $-\int_{T_s}^T c_s dT$ .

2. Transform the superconducting phase into the normally conducting phase isothermally by application of the magnetic field  $H_c$ ; this requires the supply of heat  $Q$  and the performance of work  $\frac{1}{2} V H_c^2$  (see Chaps. 13 and 14).

3. Heat the normally conducting phase in the magnetic field  $H_c$  from  $T$  to  $T_s$ , for which we have to supply heat amounting to  $\int_T^{T_s} c_N dT$ .

4. Remove the magnetic field and transform the material at  $T_s$  into the superconducting state. This step requires no heat and no work. By equating the sum of all these amounts of heat and work to zero we obtain eq. 17-13.

If Fig. 1-4 is correct,  $H_c$  for lead increases to almost 1000 oersteds,  $V$ , the quotient of the mass of one mol, 207 g, and the density, 11.3 g/cm<sup>3</sup>, is about 18.5 cm<sup>3</sup>. Therefore  $f_N - f_s = 7.5 \times 10^5$  erg =  $1.8 \times 10^{-2}$  cal.

For comparison we may mention that the difference of free energies of water and ice per mol is about  $1.6 \times 10^6$  erg at 0°C and approximately

$10^6$  dynes/cm<sup>2</sup> pressure; and  $4.6 \times 10^9$  erg at  $-20^\circ\text{C}$  and about  $1.9 \times 10^9$  dynes/cm<sup>2</sup>.<sup>7</sup>

In the neighborhood of the transition temperature, where  $H_c$  is smaller by one or two powers of 10,  $1/\kappa - f_s$  is smaller by two to four powers of 10 and therefore quite small compared with the above values for water and ice.

Using the equation for the transition curve from which Fig. 1-4 was drawn,

$$H_c = a(T^2 - T^2), \quad a = 17.3 \text{ oersted/deg}^2, \quad T_s = 7.5^\circ$$

Calculating the maximum of the heat of transition at  $5.2^\circ$  and the difference between the specific heats at the transition temperature, we find:

$$Q_{\text{max}} = 6.2 \times 10^5 \text{ erg} = 1.5 \times 10^{-2} \text{ cal} \quad (\text{lead})$$

and

$$(c_N - c_S)T_s = 6.9 \times 10^5 \text{ erg/deg} = 1.6 \times 10^{-2} \text{ cal/deg} \quad (\text{lead})$$

These figures at least give some idea of the magnitude of the values under discussion.

(f) The Rutgers-Gorter-Casimir equations 17-5, 17-9, 17-10, and 17-12 have been confirmed for several metals. We may mention here the measurements on Zn by Keesom and van Laer.<sup>8</sup> In Fig. 17-2 the points  $\circ$  show the experimental results for the molar heat found in the absence of a magnetic field. Starting above the transition temperature  $T_s$ , these points at first lie on the curve of  $c_N$  against  $T$ . At the transition temperature,  $3.7^\circ\text{K}$ , the points suddenly jump to higher values and trace the curve for  $c_S$ . The points  $\bullet$  were measured in the presence of a field of 299 oersteds, and the points  $\Delta$  in a field of 139 oersteds. As these fields prevented the appearance of superconductivity, all these points lie on the curve for  $c_N$  which apparently does not depend on the field strength. This is an important confirmation of our assumption that the thermodynamic functions of the normal conductor are uninfluenced by a magnetic field. Although  $c_S$  lies much higher than  $c_N$  at the transition temperature, the two curves intersect each other at  $1.9^\circ$  as required in section (c).

The authors were able to represent the  $c_S$  curve by Debye's law for molar heat:

$$c_S = 464.5 \left( \frac{T}{\theta_S} \right)^3 \text{ cal deg}^{-1}, \quad \theta_S = 140^\circ \quad (17-17)$$

However, in order to obtain a good representation of  $c_N$  they had to add to the  $T^3$  term a linear term in  $T$ :

$$c_N = 464.5 \left( \frac{T}{\theta_N} \right)^3 + 4 \times 10^{-1} T \text{ cal deg}^{-1}, \quad \theta_N = 185^\circ \quad (17-18)$$

In fact, even with this additional term there are still discrepancies above  $3.5^\circ\text{K}$ . The second term may be interpreted as the specific heat of the conduction electrons on the Sommerfeld theory of metallic conductivity.

<sup>7</sup> Calculated as the product of pressure and change of volume.

<sup>8</sup> W. H. Keesom and P. H. van Laer, *Physica*, 6, 193 (1938). The value  $\theta_s = 140^\circ$  was taken from their Fig. 2.

The difference  $c_N - c_S$  is thus of the form  $\alpha T^3 + \beta T$ . This leads to the parabola for  $H_c$  as a function of  $T$ , by eq. 17-12 and the conditions  $dH_c/dT = 0$  at  $T = 0$  and  $H_c = 0$  at  $T = T_s$ . The authors also emphasize that eq. 17-12 is well satisfied if their measurements are combined with those of de Haas and Engelke<sup>9</sup> on  $H_c$ .

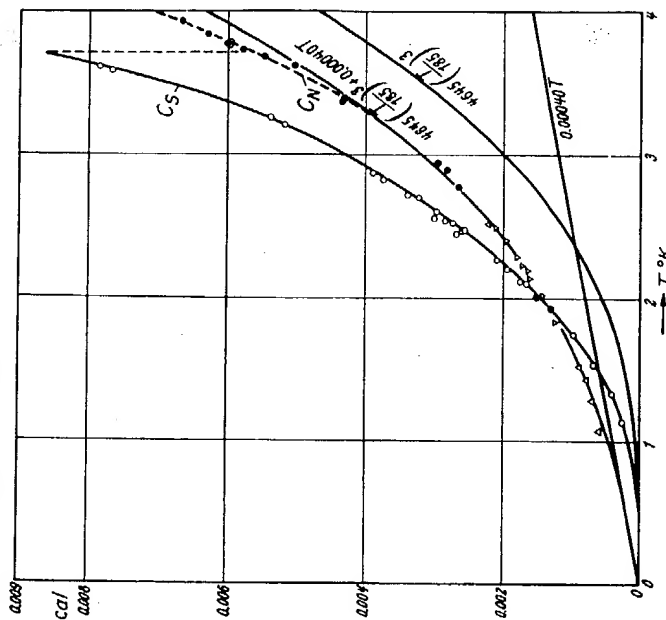


Fig. 17-2. Atomic heat of normal and superconducting tin as a function of temperature.

The jump in the atomic heat of tin at  $T_s$  is  $1.26 \times 10^5$  erg/deg  $= 3.0 \times 10^{-3}$  cal/deg, according to Fig. 17-2, and so considerably smaller than that found in lead [section (e)]. In addition to the  $1/N$  and  $f_s$  curves in Fig. 17-1 we have also plotted the entropy difference, using the values from eqs. 17-17 and 17-18:

<sup>9</sup> W. J. de Haas and Miss A. D. Engelke, *Physica*, 4, 325 (1937).

$$-(s_N - s_S) = \int_0^{T_c} \frac{1}{T} (c_N - c_S) dT \quad (17-19)$$

and also the heat of the transformation  $Q = T(s_N - s_S)$ .

Keesom and van Laer<sup>10</sup> examined the validity of eq. 17-3 by measuring the heat of transformation  $Q$  and the specific heats of tin. They find agreement between calculated and measured values of  $Q$  to within 5% in the least favorable case. The confirmation of eq. 17-19 in the same paper shows that the assumption of a reversible phase transition is justified.

(g) A homogeneous magnetic field does not generally need to have the full strength  $H_c$  in order to quench the superconductivity of any body placed in it. As shown in Chaps. 9 to 11 for many examples, and depicted in Fig. 1-5, the distortion of the field by the superconductor produces an intensification of the field at the surface of that body. This suffices for the quenching of the superconductivity if the intensification raises the field at some point to beyond  $H_c$ . If we write  $\alpha$  for the ratio of the maximum field strength at the surface to the field strength at a great distance from the specimen, the critical value of this latter field is  $H_c/\alpha$ . In the sequel we must distinguish carefully between this value, depending on the form of the specimen, and the critical  $H_c$  that depends only on the material of the specimen and the temperature.

For a "thick" elliptical cylinder with axes  $a$  and  $b$ , the  $a$  axis forming the angle  $\theta$  with the direction of the field we have, by eq. 10-24:

$$\alpha = \left( \frac{1}{a} + \frac{1}{b} \right) \frac{1}{\sqrt{a^2 \sin^2 \theta + b^2 \cos^2 \theta}} \quad (17-20)$$

The intensification factor  $\alpha$  therefore varies with  $\theta$  between  $1 + b/a$  and  $1 + a/b$ . This has been confirmed at least qualitatively by de Haas and Casimir-Jonker [Chap. 1 (f)]. For the thick circular cylinder  $\alpha = 2$ , for the "thick" sphere  $\alpha = 3/2$ , see Chap. 11.

## CHAPTER 18

### The Critical Magnetic Field for Thin Superconductors

(a) It is only for "thick" superconductors that the field strength  $H_c$  defined in eq. 17-5 is a critical value exceeding which at any point of the free surface would destroy the superconductivity. Equation 7-37 between current density and magnetic field strength at the surface holds only for a fully developed protective layer. For "thin" superconductors in which the protective layer is not fully developed, we have to go back to the more

<sup>10</sup> W. H. Keesom and P. H. van Laer, *Physica*, 3, 371 (1936).

general equations 17-3 and 17-4. These equations, remembering eq. 17-5, can be written:

$$\begin{aligned} (\mathbf{i} \cdot \mathbf{G}) &= H_c^2, & \text{equilibrium condition for the boundary between} \\ & & \text{superconductor and normal conductor} \\ (\mathbf{i} \cdot \mathbf{G}) &\leq H_c^2, & \text{condition for preserving superconductivity} \\ & & \text{at a free surface} \end{aligned} \quad (18-1)$$

In what follows we discuss cubic crystal superconductors with  $(\mathbf{i} \cdot \mathbf{G}) = \lambda i^2$ . However, the results are qualitatively valid for other forms.

Consider two geometrically similar thin superconductors of the same material and at the same temperature such that the linear dimensions of the smaller specimen can be obtained from those of the larger one by multiplication by the factor  $\alpha < 1$ . Let the two specimens be placed in the same homogeneous magnetic field  $H^0$ , then the ratio of the current density  $i$  in the smaller specimen to that at the corresponding point in the larger specimen is, according to Chap. 7 (f) equal to  $\alpha$ .

Since it is proportional to  $H^0$  we have to increase  $H^0$  by the factor  $\alpha^{-1}$  to get the same stress  $\frac{1}{2} \lambda i^2 = \frac{1}{2} H_c^2$  at corresponding points on the surface of the smaller specimen. The critical value of  $H^0$  needed to quench superconductivity increases by the factor  $\alpha^{-1}$  when the dimensions of the specimen are decreased by the factor  $\alpha$ . The smaller the disturbance of the field caused by a small superconductor, the less it is influenced by the field.

(b) We shall prove this for a few examples. For a plane parallel plate of thickness  $2d$  with field strength  $H^0$  at both sides we have by eq. 7-18

$$\lambda i^2 = (H^0)^2 \tanh^2 \beta d$$

According to eq. 18-1 the superconductivity is quenched at the critical value  $H^0 = H_c \coth \beta d > H_c$  (18-2)

For a "thick" plate this is approximately (18-3)

$$H^0 = H_c (1 + 2e^{-2\beta d})$$

and for a "thin" one

$$H^0 = H_c \frac{[1 + (\beta d)^2/3]}{\beta d} \quad (18-4)$$

The denominator  $\beta d$  corresponds to the factor  $\alpha$  in the theorem of (a).

The current density at the surface of a cylinder of radius  $R$  in a longitudinal field  $H^0$  is, according to eq. 10-2, given by:

$$\lambda (i^2)_R^2 = (H^0)^2 \left[ -\frac{i I_1(\iota \beta R)}{I_0(\iota \beta R)} \right]^2$$

The critical value is therefore

$$H^0 = H_c \left[ \frac{\iota I_0(\iota \beta R)}{I_1(\iota \beta R)} \right] > H_c \quad (18-5)$$

By using eq. 16-15 for the ratio of the Bessel functions for large values of  $\beta R$  we find

$$H^0 = H_c \left( 1 + \frac{1}{2\beta R} \right) \quad (18-6)$$

For small values of  $\beta R$ , however, the series 8-6 gives

$$H^0 = 2 H_c \frac{1 + \frac{1}{8}(\beta R)^2}{\beta R} \quad (18-7)$$

For a cylinder in a transverse field the current density at the surface is, by eq. 10-16, a maximum at  $\theta = \frac{1}{2}\pi$ . At this angle

$$(\dot{i}_\tau)^2_{R, \frac{1}{2}\pi} = 4(H^0)^2 \left[ -\frac{\epsilon I_1(\epsilon \beta R)}{I_0(\epsilon \beta R)} \right]^2$$

This value is four times the value for longitudinal fields. Therefore we have simply to divide the right-hand sides of eqs. 18-5, 18-6, and 18-7 by 2 to get the corresponding results for the transverse field.

The current density at the surface of a sphere of radius  $R$  has a maximum on the equatorial plane  $\theta = \frac{1}{2}\pi$ . According to eqs. 11-1, 11-9, and 11-5 we have

$$\lambda (\dot{i}_\tau)^2_{R, \frac{1}{2}\pi} = (H^0)^2 \left\{ \frac{3}{2} [\coth \beta R - (\beta R)^{-1}]^2 \right\}$$

A homogeneous field can therefore be increased without destroying the superconductivity only as far as the critical value:

$$H^0 = \frac{3}{2} H_c [\coth \beta R - (\beta R)^{-1}]^{-1} > \frac{2 H_c}{3} \quad (18-8)$$

This means for  $\beta R \gg 1$ , up to

$$H^0 = \frac{2}{3} H_c \left( 1 + \frac{1}{\beta R} \right) \quad (18-9)$$

while with  $\beta R \ll 1$ , up to

$$H^0 = 2 H_c \frac{1 + \frac{1}{15}(\beta R)^2}{\beta R} \quad (18-10)$$

The denominator  $\beta R$  in eqs. 18-7 and 18-10 again corresponds to the  $a$  factor in the theorem of section (a).

(c) We follow these examples by three paradoxes. At the two boundaries  $z = \pm d$  of a plane parallel plate of thickness  $2d$  carrying current  $i$  per centimeter, the current density and magnetic field are given by eq. 7-21:

$$|\dot{i}_z| = \frac{1}{2} \beta I \coth \beta d, \quad |\dot{H}_y| = \frac{I}{2c}$$

The critical value of  $i$  that quenches superconductivity is such that  $\lambda \dot{i}_z^2 = H_c^2$ . Therefore the critical current and the corresponding field intensity are respectively

$$i = 2c H_c \tanh \beta d, \quad |\dot{H}_y| = H_c \tanh \beta d \quad (18-11)$$

The critical current therefore decreases with decreasing  $\beta d$  finally going to zero; the same is true of the corresponding magnetic field. The mean critical current density, however, namely,

$$\frac{i}{2d} = \frac{H_c \tanh \beta d}{\sqrt{\lambda}} \quad (18-12)$$

increases to a maximum value  $H_c/\sqrt{\lambda}$ .

The current density at the surface of a wire of radius  $R$  carrying current  $i$  is, by eq. 8-9

$$(\dot{i}_\tau)_R = \frac{\beta I}{2\pi R} \frac{\epsilon I_0(\epsilon \beta R)}{I_1(\epsilon \beta R)}$$

To find the maximum possible supercurrent we must put  $\lambda \dot{i}_\tau^2 = H_c^2$ . This gives the maximum possible mean current density

$$\frac{i}{\pi R^2} = \frac{H_c}{\beta} \frac{I_1(\epsilon \beta R)}{\sqrt{\lambda} R I_0(\epsilon \beta R)} \quad (18-13)$$

The ratio of the Bessel functions decreases more slowly than  $\beta R$ , the mean current density therefore increases, but more slowly than  $(\beta R)^{-1}$ . In particular for large  $\beta R$  we have

$$\frac{i}{\pi R^2} = \frac{2 H_c}{\beta \sqrt{\lambda} R} \left( 1 - \frac{1}{2} \beta R \right) \quad (18-14)$$

and for small  $\beta R$

$$\frac{i}{\pi R^2} = \frac{H_c}{\sqrt{\lambda}} \left[ 1 - \frac{1}{8} (\beta R)^2 \right] \quad (18-15)$$

$H_c/\sqrt{\lambda}$  is again the maximum possible current density. The magnetic field produced by this maximum current at the surface of the wire is

$$\frac{i}{2\pi c R} = \frac{H_c \epsilon I_1(\epsilon \beta R)}{I_0(\epsilon \beta R)} \quad (18-16)$$

and is thus smaller than  $H_c$ , and the more so the smaller  $\beta R$ , vanishing with  $\beta R$ . These examples do not actually contradict the theorem of section (a), because in both these cases the superconductor was not put into an already existing field. The field outside would not exist without the current  $i$ .

The above results can easily be demonstrated and generalized. The maximum possible current load is characterized by the fact that the current density attains the value  $H_c/\sqrt{\lambda}$  for which the stress is  $\frac{1}{2} \lambda i^2 = \frac{1}{2} H_c^2$  at one or more points on the surface (in both the above examples actually over the whole surface). The mean current density required for this in a "thick" superconductor is actually very small compared with  $H_c/\sqrt{\lambda}$  because of the extended protected region beneath the protecting layer. However, the mean density for a very "thin" superconductor is equal to  $H_c/\sqrt{\lambda}$  because the current is uniformly distributed over the whole cross section. It can never increase beyond this value under any circumstances,

because according to Chap. 7 the maximum current density is always at the surface. As the cross section decreases toward zero, the maximum possible current and the magnetic field at the surface produced by this current also decrease toward zero. This is shown by eqs. 18-11 and 18-12 for a wire and eqs. 18-14, and 18-16 for a plate.

(d) The third of the mentioned paradoxes is of a different kind. If the bore of a hollow thick cylindrical superconductor contains a magnetic field  $H^0$ , then according to eqs. 10-7 and 10-6 the current on the walls is given by

$$\lambda i_{\phi} s^2 = (H^0)^2 \left[ \frac{H_1(\iota\beta R)}{\iota H_0(\iota\beta R)} \right]^2$$

To make this equal to  $H_c^2$  we must have<sup>1</sup>

$$H^0 = -H_c \frac{\iota H_0(\iota\beta R)}{H_1(\iota\beta R)} \quad (18-17)$$

The factor multiplying  $H_c$  is less than unity and is smaller the smaller  $\beta R$ . Whereas for large  $\beta R$  we have

$$H^0 = H_c \left( 1 - \frac{1}{2\beta R} \right) \quad (18-18)$$

for indefinitely decreasing values of  $\beta R$  the maximum possible value of  $H^0$  goes to zero according to the equation

$$H^0 = -H_c \beta R \log \beta R$$

This decrease with decreasing  $\beta R$  is again no contradiction to section (a), as we are not considering a "thin" superconductor.<sup>2</sup>

As already mentioned in Chap. 12 (g), it can happen that, upon cooling down a normally conducting metal in a magnetic field, at first only an annular part of the specimen becomes superconducting. Normal conductivity remains within the bore of this ring, and a number of lines of force, or rather a certain flux of induction  $[B_n \cdot d\sigma]$  is present there. This flux must remain constant (Chap. 12) with further progress of the cooling. If the bore becomes smaller, the field intensity must increase. We see therefore that the bore cannot become arbitrarily small. The critical value of the field strength decreases with the decreasing dimensions of the bore, so that in any case a state will be reached where any further shrinking of the bore will cause the magnetic field to exceed this critical value.

(e) We now come to the measurements of the critical value for "thin" superconductors. Pontius [Chap. 1 (c)] measured the critical values of a longitudinal field for lead wires at 4.2°, i. e., 3.1° below the transition temperature. The radii of the wires were of the order of magnitude  $10^{-4}$  cm

<sup>1</sup>  $\iota H_0(\iota\beta R)$  and  $-H_1(\iota\beta R)$  are positive as mentioned in Chap. 10.

<sup>2</sup> The equations of section (b), (c), and (d) were first given by M. v. Laue in the paper already quoted: *Ann. Physik*, 82, 71, 253 (1938). An error in sign in that paper led to a wrong result for the cylinder in a transverse field. The numerical values used in section (e) are also taken from that paper.

to  $10^{-3}$  cm. Figure 18-1 shows his observations compared with a theoretical curve calculated, not from eq. 18-6, but by the somewhat more exact equation<sup>3</sup>

$$\left( \frac{H_c}{H^0} \right)^2 = 1 - \frac{1}{\beta R} + \text{terms in } \frac{1}{(\beta R)^3} \quad (18-19)$$

It has been assumed that  $H_c = 537$  oersteds, and then that  $\beta = 4.78 \times 10^4 \text{ cm}^{-1}$  to yield by eq. 6-7 the value for  $\lambda$ :

$$\lambda = 4.8 \times 10^{-31} \text{ sec}^2 \text{ in Lorentz units}$$

or by eq. 6-8 the  $4\pi$  times greater value

$$\lambda = 6.0 \times 10^{-30} \text{ sec}^2 \text{ in esu.}$$

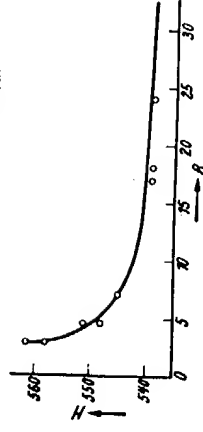


Fig. 18-1. The limiting field strength  $H^0$  in Oersteds as function of the radius  $R$  of the wire (in  $10^{-4}$  cm units) for lead at 4.2° K. The theoretical curve according to eq. 18-19 and the points observed by Pontius.

This good agreement between the calculated and observed values not only supports the theory in general, but also supports the orders of magnitude for  $\beta$  and  $\lambda$  proposed by F. London from quantum mechanical considerations. This calculation was made in 1938 and was the first one to be based on observational data.

There are also data for thin films. Shalnikov [Chap. 1 (c)] used a lead film  $1.4 \times 10^{-6}$  cm thick and a tin film  $1.1 \times 10^{-5}$  cm thick and found

<sup>3</sup> From eq. 8-7

$$-\frac{\iota I_1(\iota X)}{I_0(\iota X)} = \frac{d [\log I_0(\iota X)]}{d X}$$

and by eq. 16-10

$$I_0(\iota X) = \frac{e^X (1 + 1/8 X)}{\sqrt{2\pi X}}$$

therefore

$$-\frac{\iota I_1(\iota X)}{I_0(\iota X)} = 1 - \frac{1}{X} + \text{terms in } \frac{1}{X^3}$$

Equation 18-6 should be more exactly

$$H^0 = H_c \left[ 1 + \frac{1}{2\beta R} + \frac{3}{8(\beta R)^3} \right]$$

that the critical magnetic field strength required to quench superconductivity was far higher than the critical value  $H_c$  found for "thick" films. However, the critical current load was much smaller than that calculated from  $H_c$  on the Silsbee hypothesis. He found these results for temperatures ranging over several degrees. They correspond qualitatively with the results of sections (b) and (c). They agree also qualitatively with those of Appleyard and Misener [Chap. 1 (c)] on the critical magnetic field values in mercury films from  $4 \times 10^{-6}$  to  $1 \times 10^{-4}$  cm thick. Shalnikov's results do not seem suitable for a quantitative check of eq. 18-2 or the determination of  $\beta$  because they do not agree quantitatively with the measurements of Appleyard, Bristow, and H. London [Chap. 1 (c)] for mercury films of a similar thickness. The last mentioned authors, however, arrived at an estimate of the relative value of  $\beta$  at any  $T$  to its value at  $2.5^\circ \text{K}$  in the following manner. As the critical value depends only on the product  $\beta d$ , they selected from among their data at different temperatures and thicknesses those which yielded the same critical value. Then  $\beta d$  must have the same value for all these cases; thus

$$\frac{\beta_T}{\beta_{2.5}} = \frac{d_{2.5}}{d_T}$$

But by eq. 6-7  $\beta$  is inversely proportional to the square root of  $\lambda$ . In this way the authors found the relation between  $\sqrt{\lambda}$  and  $T$  shown in Fig. 11-3, which also shows in a striking manner the results of a completely different determination made by Shoenberg [Chap. 11 (d)].

Incidentally all these measurements of the critical magnetic field when used in eq. 18-2 to calculate  $\beta$  lead to the expected result that, sufficiently far below the transition temperature,  $\beta$  has the order of magnitude of  $10^3 \text{ cm}^{-1}$ .

(f) The whole argument of Chaps. 17 and 18 depends on the condition emphasized in Chap. 17 (a) that no current shall be entering or leaving the superconductor at the points of interest on its surface. It is only under this condition that the London stresses give rise to the tensile stress  $\frac{1}{2} \lambda i^2$  toward the interior of the superconductor. Where there is a current being supplied from outside and where  $i$  has no tangential component, the tension is replaced by a pressure of the same amount directed outwards. In general if both normal and tangential components of  $i$  exist, the force is inclined to the surface. The tangential component is exactly zero only at a few points on the surface of a "thick" superconductor. For example we saw in Chap. 8 (c) that in a superconducting cylinder of radius  $R$  to which a current is supplied through a normally conducting cylinder of the same thickness, the tangential component  $i_t$  almost everywhere over the interface greatly exceeds the normal component  $i_n$  as long as  $\beta R \gg 1$ . Only on the axis  $r = 0$  and at the circumference  $r = R$  is  $i_t = 0$ . Only in areas around these radii of extension  $\beta^{-1}$  is  $i_t \gg i_n$ .

For a "thin" cylinder or more generally a "thin" superconductor of arbitrary cross section in which the supercurrent, like the ohmic current

in the normal conductor, spreads uniformly over the cross section [Chap. 7 (a)], the tangential component at the interface vanishes. At such points, provided the normally conducting leads consist of the same material as the superconductor, thermodynamic equilibrium between the two phases would depend on the condition (compare eq. 17-3)

$$-\frac{1}{2} (i \cdot G) = \frac{(i_n - i_s)}{V}$$

This condition cannot be satisfied, because at any temperature at which the superconductor can exist at all, i.e., any temperature below  $T_c$ ,  $i_n - i_s > 0$  according to Chap. 17 (e) and Fig. 17-1 whereas  $(i \cdot G)$  is positive according to Chap. 3. The current at the interface can therefore only strengthen the tendency of the superconductor to grow at the expense of the normal conductor. Certain as yet unexplained relaxation phenomena which often blur the sharpness of the phase transition may be related to this point.

## CHAPTER 19

### The Intermediate State

(a) If the superconductivity of a specimen is quenched isothermally by an increasing external magnetic field, it does not transform immediately and completely into the normally conducting state. The nearest approach to a sudden complete transition is found with straight wires in longitudinal fields. However, even in this case the resistance does not change from zero to its final value in one single jump. The transition is by no means continuous, but takes place in several separate jumps. Thus if, following Justi<sup>1</sup> one wraps around the specimen an induction coil connected with an oscillograph or a telephone, and subjects the specimen to a continuously increasing magnetic field, one observes current impulses caused by sudden large changes in the flux of induction.

In other cases where the transition is much slower it can be followed through all its intermediate stages by placing minute bismuth wires inside cavities in the specimen and measuring their resistance as a function of the external field, as was done by de Haas and his collaborators. The resistance of bismuth changes in a known manner with the local magnetic field strength. This arrangement, which naturally is limited to thick superconductors, demonstrates the gradual penetration of the external field. It is impossible for a normally conducting shell to form either completely or partly round a superconducting core. The thermodynamics of Chap. 17 requires the existence of the critical magnetic field  $H_c$  corresponding to the prevailing

<sup>1</sup>E. Justi, *Physik Z.*, 43, 130 (1942); *Ann. Physik*, 42, 84 (1942).

temperature at every point on the boundary between any such normal envelope and the core. On the other hand, the lines of force, according to electrodynamics, must be parallel to the boundary surface. These two requirements are mathematically inconsistent.

(b) In the first place it is out of the question for the normally conducting shell to enclose the superconducting core completely. There must exist places (either curves or at least points) on the boundary surface where the incident lines of force divide sharply into two lines parallel to the surface. (For a spherical core this would occur at the poles, see Fig. 1-5.) The field strength at these points is zero according to potential theory because the field direction is indefinite, and so cannot equal  $H_c$ .

Let us confine ourselves for the moment to two-dimensional problems. Let the boundary of the core  $S$  consist of two parts  $S_1$  and  $S_2$ ; at  $S_1$  the core borders either on empty space or on a normal conductor of chemically different material, and at  $S_2$  on the normally conducting shell. Both  $S_1$  and  $S_2$  may consist of several separate sections. We assume each section to be an analytic curve i. e., they can be represented by equations of the form  $x = f(s)$ ,  $y = g(s)$  where  $f$  and  $g$  are analytic functions.

At each point where a section of  $S_1$  meets the adjacent section of  $S_2$  it is not permissible for them to form an angle with each other. Such an angle would make a kink in  $S$ ; if the kink were re-entrant the field strength, according to potential theory, would be zero; if the kink were raised (convex), the field would be extremely large (mathematically infinite); in any case it could not be equal to  $H_c$  at such kinks. The above parametric representation therefore holds uniformly over the whole boundary curve  $S$ , and therefore  $H$  on the boundary must also be an analytic function of the parameter  $s$ . As it is constant and equal to  $H_c$  over all parts of  $S_2$ , it must also be equal to  $H_c$  over  $S_1$  in spite of the fact that it must also be zero at some points.

The same inconsistency is found in the three-dimensional case. We can ascribe to any part of the boundary, whether it belongs to  $S_1$  or to  $S_2$ , an analytical representation in terms of two parameters:  $x = f(s, t)$ ,  $y = g(s, t)$ ,  $z = h(s, t)$ . No singularities are permitted at any point where sections of  $S_1$  and  $S_2$  touch, because they would cause zeros or infinities in  $H$ . Therefore the analytical representation holds uniformly over the whole boundary  $S$ . Then  $H$  is also an analytical function of  $s$  and  $t$ . Because it is constant and equal to  $H_c$  over  $S_2$ , it must also be constant over  $S_1$  in spite of the fact that places must exist where  $H = 0$ .<sup>2</sup> So if a piece of material cannot be either normally conducting as a whole nor superconducting, it must be in an "intermediate state" representing a mixture of alternating superconducting and normally conducting regions.

The difficulty discussed above for thick superconductors does not exist for small superconducting regions dispersed through a normal conductor, because such small regions do not disturb the magnetic field, according to

<sup>2</sup>M. v. Laue, *Physik. Z.*, **43**, 274 (1942).

Chap. 7, and are themselves barely affected by the field, according to Chap. 18.

These conclusions are confirmed by an experiment by Shubnikov and Nachutin.<sup>3</sup> They quenched the superconductivity of a sphere in a magnetic field and measured the electric resistance parallel and perpendicular to the external field before the sphere had become completely normally conducting. Long after resistance had appeared in the direction perpendicular to the field, they could find no resistance in the direction parallel to the field. This is difficult to explain except in terms of coexisting normal and superconducting regions. It suggests, moreover, that the superconducting regions are much more extended in the direction of the field than in the transverse direction. This fits in with the argument of Chap. 18 (b) according to which a cylinder or any other elongated specimen loses its superconductivity much more easily in a transverse field than in a longitudinal one.

(c) The earliest method of recognizing superconductivity was to observe the disappearance of the d-c resistance. However this method is hardly suitable for distinguishing between the superconducting and the intermediate states because the normally conducting regions will not participate in carrying the current so long as the current can find a closed path through the superconducting regions. A far better criterion for the break down of the superconducting state is the disappearance of the Meissner effect, i. e., the appearance of a magnetic field within the interior of the specimen. In this way it is possible to understand why the first measurable resistance of a wire in a transverse field has been observed at  $H^0 = 0.58 H_c$ ,<sup>4</sup> whereas according to theory [Chap. 18 (b)] and the experiments to be mentioned immediately, superconductivity is already destroyed when  $H^0 = 0.50 H_c$ .

In order to observe the field penetration, de Haas and Casimir-Jonker<sup>5</sup> inserted minute bismuth wires, as described above, in holes in a tin wire 0.7 cm in diameter, see Fig. 19-1. They measured the increase of resistance of the bismuth wires while gradually increasing the external magnetic field  $H^0$ . Figure 19-2 shows the results when the plane of the wires is perpendicular to the field  $H^0$ ; Fig. 19-3 when it is parallel. The critical value  $H_c$  can be recognized in both diagrams at the point where the resistance curves meet the resistance curve of a bismuth wire exposed to the external field  $H^0$ , and indicated in Fig. 19-2 by the dotted line. This point is where the specimen allows the external field to penetrate it completely. In Fig. 19-2

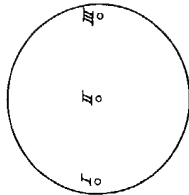


Fig. 19-1. Cross section through tin cylinder with bismuth probe wires inserted at I, II, and III. (After W. J. de Haas and J. M. Casimir-Jonker.)

<sup>3</sup>L. Shubnikov and J. Nachutin, *J. Exp. Theoret. Phys. (U.S.S.R.)*, **7**, 566 (1957).

<sup>4</sup>W. J. de Haas, J. Voogd, and J. M. Casimir-Jonker, *Physica*, **1**, 281 (1934).

<sup>5</sup>W. J. de Haas, and J. M. Casimir-Jonker, *Physica*, **1**, 291 (1934).

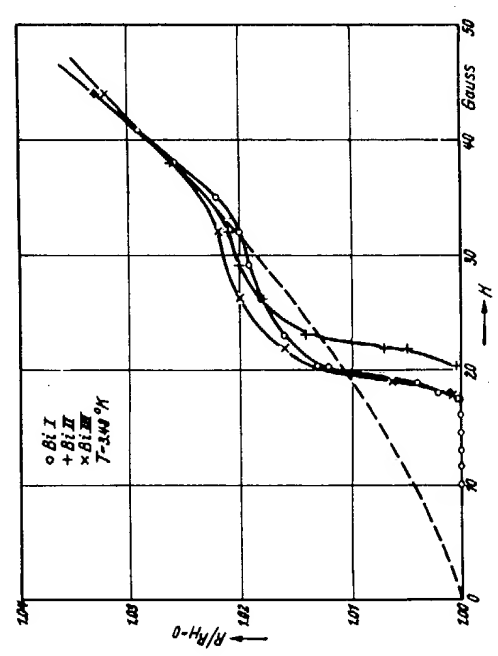


Fig. 19-2. Increase of resistance in the bismuth probe wires due to penetration of a magnetic field normal to the plane of the wires.

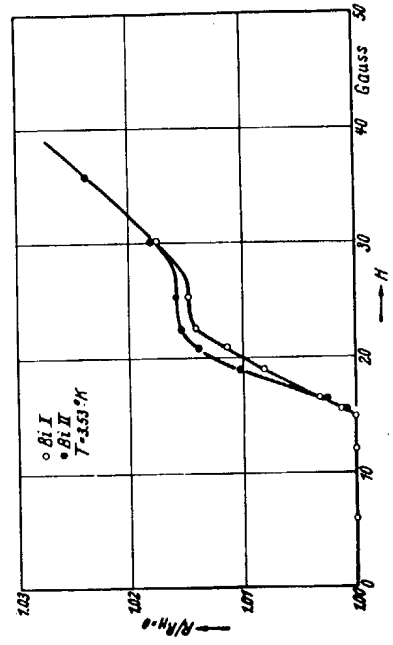


Fig. 19-3. Increase of resistance in the bismuth probes due to penetration of a magnetic field parallel to the plane of the wires.

$H_c$  falls at about 36 oersteds; in Fig. 19-3 at about 30 oersteds because of the slightly higher temperature. One sees that the first sign of the field penetration occurs in both diagrams at the field  $H^0 = \frac{1}{2} H_c$ , i. e., at 18 and 15 oersteds respectively, as required by theory. The wire II was placed in the axis of the wire, so the fact that its curve reacted only at 20 oersteds does not alter the fact that both the wires I and III, placed nearer the outside of the wire, show the breakdown of superconductivity already at 18 oersteds.

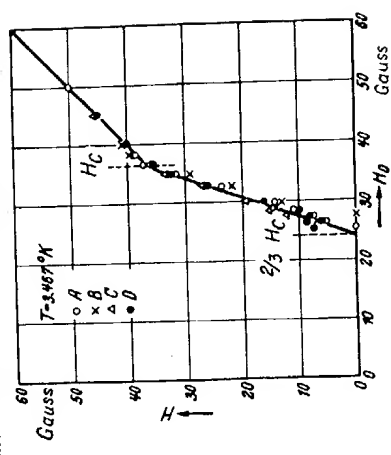
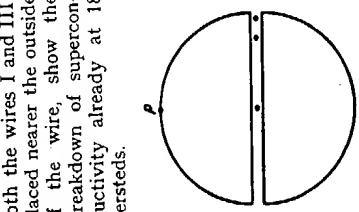


Fig. 19-4. Cross section of a tin sphere cut across an equatorial plane with bismuth wires inserted at the poles shown. (After W. J. de Haas and O. A. Guineau.)

Fig. 19-5. Magnetically induced isothermal transition from super- to normal conduction in a single crystal tin sphere. Points marked A, B, C represent magnetic field strengths shown by the bismuth probes of Fig. 19-4, D the field strength at the pole P of the sphere.

The theory has been confirmed more exactly for the case of a sphere where, according to Chap. 18 (b) the critical value should be  $H^0 = \frac{2}{3} H_c/3$ . de Haas and Guineau<sup>6</sup> cut a tin sphere (1.65 cm in diameter) into two hemispheres and placed them 0.03 mm apart (Fig. 19-4). In the space between the two halves they placed three bismuth wires, one in the center, the second 0.55 cm and the third 0.75 cm from the center. The field strengths calculated from the resistance decrease in the bismuth wires are shown in Fig. 19-5 as a function of  $H^0$  which in this experiment was perpendicular to the plane of the cut. The magnetic field strength at the pole P of the sphere is also plotted. All four curves coincide exactly. They start at 24 oersteds, and at 36 oersteds they join the straight line  $H = H^0$ , indicating that the protective influence of the tin sphere has completely disappeared. Thus the critical value  $H_c$  is 36 oersteds, and the limiting value  $H^0$  for superconductivity is  $\frac{2}{3} H_c$ .

<sup>6</sup>W. J. de Haas and O. A. Guineau, *Physica*, 8, 182 (1956).



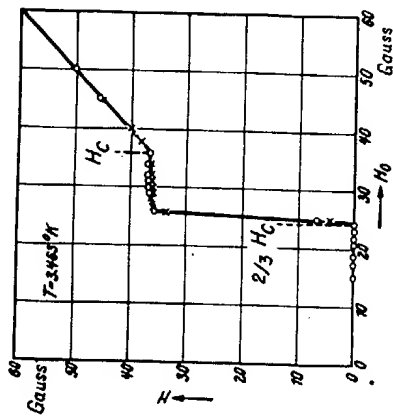


Fig. 19-6. Magnetically induced isothermal transition from super- to normal conduction of a single crystal tin sphere. The field strengths are measured in a hole bored through the center of the sphere parallel to the field.

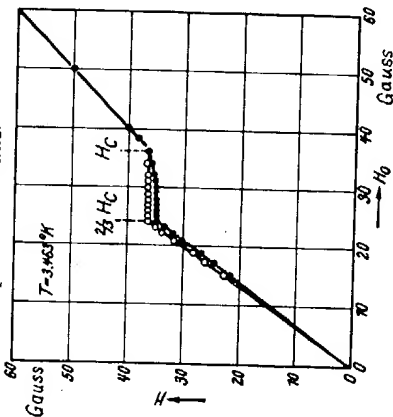


Fig. 19-7. Magnetically induced isothermal transition from super- to normal conduction in a single crystal tin sphere. O-field strength exactly on the equator of the sphere; ●-field strength at a point on the plane of the equator slightly outside the sphere.

This is further confirmed by experiments represented in Fig. 19-6, in which the bismuth wires were placed inside a channel parallel to the field through the center of the sphere to measure the field penetration. The field jumps almost discontinuously to the value 36 oersteds when the external field reaches the value 24 oersteds, and remains practically constant until  $H^0$  also reaches the value 36 oersteds. From then on the sphere no longer disturbs the field, and it follows the line  $H = H^0$ .

Figure 19-7 explains why the field jumps immediately to 36 oersteds in spite of the fact that  $H^0$  is still smaller than this value. In this experiment two bismuth wires were placed in the equatorial plane, one exactly on the equator of the sphere (which was not cut like the one in Fig. 19-6), the other a little above the surface of the sphere. In this case the measured field  $H$  follows a straight line  $H = 3 H^0/2$  and shows the intensification of the field at the equator of a superconducting sphere (Chap. 11 [6]). At  $H^0 = 24$ , and  $H = 36$  oersteds, however, the superconductivity breaks down, and  $H$  at first remains constant at this value as shown in Fig.

19-6. As soon as  $H^0$  also reaches 36 oersteds the undisturbed field  $H^0$  exists throughout the sphere, as shown again in this diagram.

The experiments represented in Figs. 19-4 and 19-5 have been repeated by Meshkowsky and Shalnikov<sup>7</sup> with a considerably narrower slit. Also instead of three fixed bismuth wires they used a movable bismuth probe which they displaced continuously along the diameter, registering field strengths at each position. For wider slits and relatively thick bismuth probes they confirmed the results of Fig. 19-5. But with an especially thin slit, namely,  $1.2 \times 10^{-2}$

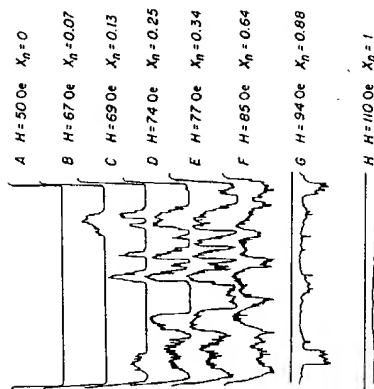


Fig. 19-8. Magnetic field strength as function of position within a narrow equatorial slit in a single crystal tin sphere measured by movable bismuth probes, according to Meshkowsky and Shalnikov.

increase in number with increasing  $H^0$ . At  $H^0 = 94$  oersteds (curve G) the field has penetrated the sphere almost completely, and at  $H^0 = 110$  oersteds it has the same value inside as outside the sphere.

The authors emphasize the fact that it is impossible to reproduce the curves exactly, although their general character remains the same with repeated experiments. The irregularity of the intermediate state is demonstrated by the accidental form of the field distribution.

<sup>7</sup>A. Meshkowsky and A. Shalnikov, *J. Physics (U.S.S.R.)* **11** (1947).

(b) We shall not change any of the fundamental equations enumerated in Chap. 3 except the relation between supercurrent density  $\mathbf{j}$  and the supercurrent momentum  $\mathbf{G}$ , i. e., we abandon eqs. VIII and VIII a, but retain all the other equations indicated by roman numerals. The new relation will be left open to a considerable extent, it being required only that it shall be uniquely reversible and go over to the linear relation VIII (or VIII a) for sufficiently weak currents; that a change of sign of  $\mathbf{j}$  shall cause a change of sign of  $\mathbf{G}$ , and the angle between  $\mathbf{j}$  and  $\mathbf{G}$  shall always be acute so that

$$(\mathbf{j} \cdot \mathbf{G}) > 0 \quad (20-1)$$

For a given direction of  $\mathbf{j}$  the absolute value of  $\mathbf{G}$  and the absolute value of  $\mathbf{j}$  increase simultaneously.

The most important restriction, however, arises from the energy principle. Equation 5-4 can be taken over immediately, and by eq. IX we can put in that equation

$$(\mathbf{E} \cdot \mathbf{j}) = \left( \mathbf{j} \cdot \frac{\partial \mathbf{G}}{\partial t} \right) \quad (20-2)$$

We require that the integral

$$F \equiv \int \left( \mathbf{j} \cdot \frac{\partial \mathbf{G}}{\partial t} \right) dt \quad (20-3)$$

shall depend only on the final supercurrent density when the latter is zero at the beginning, being independent of the intermediate states through which it has passed. Owing to the assumption of unique reversibility of the relation between  $\mathbf{j}$  and  $\mathbf{G}$  we can also state that  $F$  depends only on the momentarily existing supercurrent momentum  $\mathbf{G}$ , or alternatively, that the integral

$$F_2 = \int_0^G (\mathbf{j} \cdot d\mathbf{G}) \quad (20-4)^2$$

shall be independent of the path of integration in  $\mathbf{G}_a$  space. Otherwise the theory would lead to energy transformations within the superconductor contradictory to observation. Under these conditions eq. 20-4 becomes the definition of the density of free energy  $F_2$  associated with the supercurrent. The mathematical expression for these conditions is:

$$\frac{\partial F_2}{\partial \mathbf{G}_\beta} - \frac{\partial F_2}{\partial \mathbf{G}_\alpha} = 0 \quad (\alpha, \beta = 1, 2, 3) \quad (20-5)$$

This ensures that the integral appearing in the equation

<sup>2</sup> In the integrand it is to be understood that  $\mathbf{l}$  and  $\mathbf{g}$  are variables of integration that assume the values  $\mathbf{j}$  and  $\mathbf{G}$  at the upper limit. The relation between  $\mathbf{l}$  and  $\mathbf{g}$  is naturally the same as between  $\mathbf{j}$  and  $\mathbf{G}$ .

## CHAPTER 20

### A Nonlinear Extension of the Theory<sup>1</sup>

(a) According to Chap. 17 the breakdown of superconductivity becomes inevitable for thermodynamic reasons as soon as the energy density  $\frac{1}{2}(\mathbf{j} \cdot \mathbf{G})$  reaches the critical value  $f_c(w - f_c)/V$  at any point of the surface, the transformation into the normally conducting phase starting at that point (eq. 17-4). For a "thick" superconductor, we can, according to eq. 7-37 put  $\frac{1}{2}(\mathbf{j} \cdot \mathbf{G}) = \frac{1}{2}H_0^2$  and this leads to the critical value of the magnetic field strength given by eq. 17-5. However, the atomic theory of superconductivity recently developed by Heisenberg<sup>2</sup> leads to the idea of a maximum density of the supercurrent that cannot be exceeded because of quantum theoretical restrictions. The question arises: Is this a new stability condition for the superconducting phase? Is the breakdown of superconductivity possible from within, and how is this related with thermodynamics?

The maximum current density  $\mathbf{j}_m$  like the critical magnetic field strength  $H_c$  must be a function of temperature. They are both zero at the transition temperature  $T_c$ . Also  $\mathbf{j}_m$  is zero at absolute zero temperature and has a maximum, according to current estimates, in the neighborhood of  $\frac{1}{2}T_c$ . According to Chap. 1, Fig. 1-4, the critical field  $H_c$  increases continuously with decreasing temperature. This different behavior emphasizes the importance of the following question: If the maximum current density, and therefore for a wire of given thickness the maximum total current, decreases toward zero with decreasing temperature, how can the supercurrent produce the field strength at the surface required by thermodynamics for the breakdown of superconductivity?

There is no upper limit to the current density in the theory so far presented in this book. We shall make it possible to include such a maximum current by means of a nonlinear extension of the theory without sacrificing very many of its results. This step was also suggested by the fact that experimentalists have for some time doubted whether the penetration depth of a transverse field in a wire is actually independent of the field strength in the manner required for the theory of Chap. 9.\*

<sup>1</sup> Compare the following references:

- M. v. Laue, *Ann. Physik*, (6) 5, 197, 1949.  
 W. Heisenberg, (a) *Z. Naturforsch.*, 2a, 185 (1947); (b) *Z. Naturforsch.*, 8a, 65 (1948);  
 (c) *Göttingen Nachr. Math.-Physik. Klasse*, 1947, p. 23; (d) *Ann. Physik*, 8, 289 (1948).  
 H. Koppe, (a) *Z. Naturforsch.*, 4a, 79 (1949); (b) *Ergeb. exakt. Naturw.*, 28, 283, (1950).

\* See Heisenberg reference in footnote 1.

\* Compare A. B. Pippard, *Proc. Roy. Soc. A* 208, 195, 210, (1950).

$$F^s = (\mathbf{i} \cdot \mathbf{G}) - \int_0^{\mathbf{i}} (\mathbf{g} \cdot d\mathbf{i}) \quad (20-6)$$

shall be independent of the path of integration in  $\mathbf{i}_s$  space and leads to conditions equivalent with eq. 20-5, namely,

$$\frac{\partial G_\alpha}{\partial i_\beta} - \frac{\partial G_\beta}{\partial i_\alpha} = 0 \quad (\alpha, \beta = 1, 2, 3) \quad (20-7)$$

From eq. 20-1 it then follows that

$$F^s > 0 \quad (20-8)$$

Equation 20-4 may now be integrated in  $\mathbf{G}_s$  space along the straight line that connects the origin (zero  $\mathbf{G}$ ) with the end of the vector  $\mathbf{G}$ . On this line increments  $d\mathbf{G}_s$  are proportional to  $\mathbf{G}_s$  and have the same sign, so that  $(\mathbf{i} \cdot d\mathbf{g}) > 0$  along the whole path. The same argument applied to the  $\mathbf{i}_s$  space proves that the integral in eq. 20-6 is positive. It therefore follows that

$$F^s < (\mathbf{i} \cdot \mathbf{G}) \quad (20-9)$$

The surfaces  $F^s = \text{constant}$  will be closed shells in both  $\mathbf{G}_s$  space and in  $\mathbf{i}_s$  space. They will have the same symmetry as that of the crystal class about the origin as center. As long as the linear approximation VIII holds, eq. 20-7 goes over into the symmetry condition  $\lambda_{\alpha\beta} = \lambda_{\beta\alpha}$ , and the surfaces are ellipsoids or spheres for the cubic system. In the general case they have less simple forms, and in general  $\mathbf{i}^s$  and  $\mathbf{G}$  are different in direction even for the cubic system. If  $\mathbf{i}^s$  happens to coincide in direction with an axis of rotation,  $\mathbf{G}$  must do the same because of the uniqueness of their relationship, and of course this is true for any crystal class.

The possibility cannot be excluded that there exists a surface in  $\mathbf{i}_s$  space, at a finite distance from the origin, corresponding to infinite free energy  $F^s = \infty$ . The vector  $\mathbf{i}^s$  could then never grow beyond that surface, and there would exist a maximum current density dependent on direction. At such a surface  $\mathbf{G}$  would also become infinite, for otherwise  $F^s$  must remain finite by eq. 20-9. Under these circumstances the energy principle (compare eq. 5-5) takes the form

$$\frac{\partial}{\partial t} \left\{ \frac{1}{2} \mathbf{E}^2 + \frac{1}{2} \mathbf{H}^2 + F^s \right\} + (\mathbf{i}^s \cdot \mathbf{E}) + c \operatorname{div} [\mathbf{i}^s \times \mathbf{H}] = 0 \quad (20-10)$$

Just as in Chap. 5, we can conclude from this that space charges in a superconductor compensate each other in a short time, or move to the surface until the total density  $\rho = \rho^0 + \rho^s$  vanishes. We do not learn anything from this theory about  $\rho^s$  itself.

By integrating the integral in eq. 20-6 along the same straight line in  $\mathbf{i}_s$  space one can put

$$(\mathbf{g} \cdot d\mathbf{i}) = \left[ \frac{(\mathbf{g} \cdot \mathbf{i})}{|\mathbf{i}|} \right] d|\mathbf{i}|$$

For the linear theory the component  $(\mathbf{g} \cdot \mathbf{i})/|\mathbf{i}|$  of the vector  $\mathbf{g}$  in the direction  $\mathbf{i}$  becomes proportional to  $|\mathbf{i}|$ , as shown by the straight line in Fig. 20-1. We then find (in agreement with eq. 5-6)

$$\int_0^{\mathbf{i}} (\mathbf{g} \cdot d\mathbf{i}) = \frac{1}{2} (\mathbf{G} \cdot \mathbf{i}^s), \quad F^s = \frac{1}{2} (\mathbf{G} \cdot \mathbf{i}^s)$$

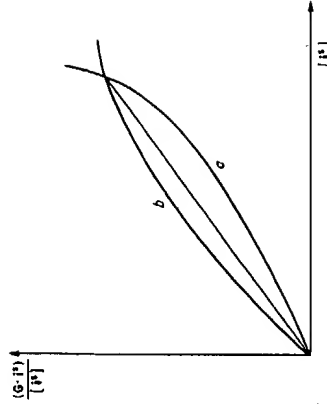


Fig. 20-1. Schematic representation of the types of nonlinear relations between supercurrent momentum  $\mathbf{G}$  and supercurrent density  $\mathbf{i}^s$ . Abscissa: magnitude of the supercurrent  $\mathbf{i}^s$ . Ordinate: component of supercurrent momentum in direction of the supercurrent.

In the nonlinear theory the relation between  $(\mathbf{g} \cdot \mathbf{i})/|\mathbf{i}|$  and  $|\mathbf{i}|$  can be represented for example by a curve of the type  $a$  in Fig. 20-1. Then clearly

$$\int_0^{\mathbf{i}} (\mathbf{g} \cdot d\mathbf{i}) < \frac{1}{2} (\mathbf{G} \cdot \mathbf{i}^s), \quad F^s > \frac{1}{2} (\mathbf{G} \cdot \mathbf{i}^s) \quad (20-11)$$

while for a curve of the type  $b$  in Fig. 20-1 we would have

$$\int_0^{\mathbf{i}} (\mathbf{g} \cdot d\mathbf{i}) > \frac{1}{2} (\mathbf{G} \cdot \mathbf{i}^s), \quad F^s < \frac{1}{2} (\mathbf{G} \cdot \mathbf{i}^s) \quad (20-12)$$

The existence of a maximum current density corresponds to the case  $a$  because here  $\mathbf{G}$  increases more rapidly than proportionally to  $\mathbf{i}^s$ .

(c) We now have to find out to what extent the results of the linear theory still apply, and we start with the Meissner effect.<sup>4</sup>

<sup>4</sup>The equation 7-4 is still valid because in proving it the relation between  $\mathbf{G}$  and  $\mathbf{i}^s$  is never used. However we cannot take over the proof of the uniqueness theorem following eq. 7-4 because the difference field between two possible fields is no longer itself a possible field, i. e., one that satisfies the fundamental equations.

Let us first consider, as in Chap. 7, the stationary state with all field quantities depending only on  $x_3$ . Because of  $\text{div } \mathbf{i} = 0$  and  $\text{div } \mathbf{H} = 0$ , we get as before  $i_3 = 0$ ,  $H_3 = 0$ , but  $G_3$  is generally different from zero. Equation X, under this assumption, yields

$$-\frac{dG_1}{dx_3} = H_2, \quad \frac{dG_2}{dx_3} = H_1 \quad (20-13)$$

whereas from II,

$$-i_1' = c \frac{dH_2}{dx_3}, \quad i_2' = c \frac{dH_1}{dx_3} \quad (20-14)$$

Elimination of  $\mathbf{H}$  leads to the partial differential equations

$$c^2 \frac{d^2 G_1}{dx_3^2} = i_1', \quad c^2 \frac{d^2 G_2}{dx_3^2} = i_2' \quad (20-15)$$

in which  $G_1$  and  $G_2$  have to be regarded as functions of  $i_1'$  and  $i_2'$  respectively. These equations replace the former differential equation  $\Delta u - \beta^2 u = 0$ . Taking the product of the first of these with  $G_1$  and the second with  $G_2$  and adding the results we obtain

$$G_1 \frac{d^2 G_1}{dx_3^2} + G_2 \frac{d^2 G_2}{dx_3^2} = \frac{1}{c^2} (\mathbf{i}' \cdot \mathbf{G})$$

and by eq. 20-13:

$$\frac{d^2}{dx_3^2} (G_1^2 + G_2^2) = \frac{2(\mathbf{i}' \cdot \mathbf{G})}{c^2} + \frac{\left(\frac{dG_1}{dx_3}\right)^2}{\left(\frac{dG_2}{dx_3}\right)^2} + \left(\frac{dG_2}{dx_3}\right)^2 \quad (20-16)$$

On the other hand, if we multiply the left-hand equations of 20-13 and 20-14 together, and also the right-hand equations, and add the results, we find, by using eq. 20-4 that

$$\frac{dF_3}{dx_3} = \frac{1}{2} \frac{d(H^2)}{dx_3} \quad (20-17)$$

or, by introducing an arbitrary integration constant  $C$ ,

$$F_3 = \frac{1}{2} H^2 - C \quad (20-18)$$

Using eqs. 20-18 and 20-15 gives

$$\frac{d^2}{dx_3^2} (G_1^2 + G_2^2) = \frac{2}{c^2} [(\mathbf{i}' \cdot \mathbf{G}) + F_3 + C] \quad (20-19)$$

Here  $(\mathbf{i}' \cdot \mathbf{G})$  and  $F_3$  are to be regarded as known functions of  $i_1'$  and  $i_2'$  just as are  $G_1$  and  $G_2$ .

In order to discuss eq. 20-19, we now write  $z$  for  $x_3$  and put  $G_1^2 + G_2^2 = u(z)$ . According to eq. 20-16  $u'' > 0$ , so the curve of  $u(z)$  is everywhere concave upwards. To within the linear approximation  $(\mathbf{i}' \cdot \mathbf{G})$  as well as  $F_3$  are proportional to  $(G_1^2 + G_2^2)$ , the proportionality factor depending on the ratio  $G_1/G_2$ . In any case, on this approximation eq. 20-19 assumes the form

$$u'' = A^2(u + C')$$

where  $A$  is a constant and  $C'$  another constant proportional to  $C$ . The solution in terms of another integration constant  $B$  is

$$u + C' = B \exp [\pm A(z - z_0)]$$

We use the lower sign and choose  $C = 0$ , therefore also  $C' = 0$ . Then  $u$  and therefore also  $G_1$  and  $G_2$  approach zero with increasing  $z$ . By eqs. 20-13 and 20-14  $\mathbf{i}'$  and  $\mathbf{H}$  decrease exponentially with increasing  $z$ , in agreement with Chap. 7. However,  $(G_1^2 + G_2^2)$  increases in the negative  $z$  direction because of the positive  $u''$ , finally without limit. It depends upon the relation between  $\mathbf{i}'$  and  $\mathbf{G}$  whether  $u$  increases without limit at a finite  $z$  or only at infinite  $z$ . In any case we can, by choosing a suitable value for  $z_0$ , arrange for  $H^2 = c^2 [(dG_1/dx_3)^2 + (dG_2/dx_3)^2]$  to have any prescribed value  $H_0^2$  at  $z = x_3 = 0$ . To obtain also a prescribed direction for  $\mathbf{H}$  at the origin we must also be free to choose the ratio  $G_1/G_2$  at any point appropriately.

Let the superconductor occupy the half space  $x_3 > 0$  as in Chap. 7, while a homogeneous magnetic field  $\mathbf{H}^0$  exists where  $x_3 < 0$ . Then the solutions just discussed will yield the Meissner effect, i. e., the restriction of the magnetic field in the superconductor to a protecting layer close under the surface.

For a plane parallel plate of finite thickness,  $C$  differs from zero. Indeed  $C < 0$  if a current is passed through the plate without producing an additional magnetic field. Then  $\mathbf{H} = 0$  exactly at the center of the plate, by symmetry, but  $\mathbf{i}'$  and with it  $F_3$  are different from zero. If instead we prescribe that the magnetic field  $\mathbf{H}^0$  shall be the same at the two surfaces without passing a current through it, then  $\mathbf{i}' = 0$  but  $\mathbf{H}$  differs from zero and therefore  $C > 0$  at the middle.<sup>5</sup>

<sup>5</sup> H. Koppe (see footnote 1) integrated the differential equation under the arbitrary assumption that

$$G = \frac{\lambda \mathbf{i}'}{\sqrt{1 - \mathbf{i}'^2 / i_m^2}}$$

His result is represented in Fig. 20-2, which shows the field distribution in the superconducting half of space,  $z > 0$ . In this figure

$$i = \frac{|\mathbf{i}'|}{i_m}, \quad h = \frac{H}{\sqrt{\lambda} i_m}, \quad g = \frac{G}{c \sqrt{\lambda} i_m}, \quad w = \frac{F_3}{\lambda i_m^2}$$

the unit for  $x_3$  is  $\exp \sqrt{\lambda}$ . The boundary surface of the superconductor has to be so chosen that it coincides with the prescribed value of  $H^0$ . If this value is comparatively small, the boundary lies fairly far to the left in the diagram and the field quantities decrease exponentially with increasing  $x_3$ . If  $H^0$  is relatively large, the boundary lies far to the right and the current density in the protecting layer is not much less than  $i_m$  over a wide region.

(d) In a cylinder carrying a current (Chap. 8) the situation becomes rather complicated unless the direction of the current coincides with a crystallographic axis of rotation, so that, by section (b), the vectors  $\mathbf{G}$  and  $\mathbf{i}$  are parallel. In this case we can use simply the magnitudes  $G$  and  $i$ .

Introducing cylindrical coordinates as in Chap. 8,  $G$  and  $i$  become functions of the radius vector only. The same is true of the component of the magnetic field  $H_\theta$  in the  $\theta$  direction. Equation X then yields,

$$c \frac{dG}{dr} = H_\theta \quad (20-20)$$

and from eq. II, (compare eq. 8-1)

$$i = \frac{c}{r} \frac{d(rH_\theta)}{dr} \quad (20-21)$$

We proceed as in section (c). Eliminate  $\mathbf{H}$  and multiply the last two equations, and we then obtain

$$\begin{aligned} \frac{d}{dr} \left( r \frac{dG^2}{dr} \right) &= \frac{2r}{c^2} (G i + H_\theta^2) \\ r \frac{dG^2}{dr} &= \frac{2}{c} \int_0^r \tau (G i + H_\theta^2) d\tau \end{aligned} \quad (20-22)$$

and after integration

$$F_s = \frac{1}{2} H_\theta^2 + \int_0^r \frac{H_\theta^2}{\tau} d\tau + F_\theta^s \quad (20-23)$$

The integration constant  $F_\theta^s$  represents the energy density at the axis  $r = 0$ . According to eq. 20-22,  $dG/dr > 0$ , and this represents the Meissner effect.

Apply eq. 20-23 at the surface of the wire ( $r = R$ ) where the field is  $H^0$ . If  $R$  is large compared with a suitably defined penetration depth  $d$ , then the integral is at most of the order of magnitude  $(H^0)^2 d/R$ , and therefore small compared with  $\frac{1}{2} (H^0)^2$ . The same is true of  $F_s$ . Consequently just as in eq. 20-18 where  $C = 0$  for the "thick" superconductor,

$$F_s = \frac{1}{2} (H^0)^2 \quad (20-24)$$

However, it is possible for  $F_s \gg \frac{1}{2} (H^0)^2$ , if  $F_\theta^s \gg \frac{1}{2} H_\theta^2$ , i. e., if the current is more or less uniformly distributed over the cross section of the cylinder.

(e). London's theorems concerning persistent currents (eqs. 12-11 and 12-13) remain unchanged. The proof of these equations does not use any relation between  $\mathbf{G}$  and  $\mathbf{i}$ . Likewise eq. 12-21 is still valid; the left-hand side is still positive for any really existing field even though it no longer represents the total free energy of the field. Thus on the nonlinear theory there still exist no magnetic fields that are not produced by one of the three following causes: annular currents in a superconductor, ohmic currents in

a normal conductor, and permanent magnetism. The proof that these causes determine the field uniquely cannot be given in the same way as in Chap. 12, because now the difference field is no longer a possible field as it was in the linear theory.

(f) Sections (c) to (e) show how little the nonlinear theory differs from the linear one for stationary fields. It is difficult to decide between them on the basis of experimental evidence at present available. The decisive question is whether on the nonlinear theory there also exists a stress tensor  $\Theta$ , depending on the supercurrent density as in Chap. 13 and exerting a volume force on a homogeneous superconductor that exactly cancels the force due to the Maxwell stress tensor. The fact that the resistance vanishes demands this unequivocally.

We now proceed to prove the impulse theorem 13-10 for the nonlinear theory. The force equation

$$\Theta_{\alpha\beta} = i_\beta^s G_\alpha - \delta_{\alpha\beta} F_s \quad (20-25)$$

provides the required proof, because actually it does not differ from eq. 13-1 if we write  $P = i$ ,  $Q = G$ , because then  $F_s = \frac{1}{2} \sum i_\alpha^s G_\alpha$ . The proof follows the earlier calculation of  $\text{div } \Theta$ . The  $x_1$  component of this vector is defined in eq. 13-3, and we have to put

$$\Theta_{11} = i_1^s G_1 - F_s, \quad \Theta_{12} = i_2^s G_1, \quad \Theta_{13} = i_3^s G_1 \quad (20-26)$$

The differential coefficient  $\partial F_s / \partial x_1$  appears in the result.

$F_s$  depends both on  $i$  and on certain parameters  $p_n$  which are present also in the relation between  $\mathbf{G}$  and  $\mathbf{i}$ . The  $p_n$ 's are functions of the temperature and differ from substance to substance. Whenever the superconductor is inhomogeneous, whether due to temperature differences or to differences in chemical composition (as in alloys at soldered boundaries), the  $p_n$ 's are functions of the coordinates  $x$ . From eq. 20-4 it therefore follows that

$$\frac{\partial F_s}{\partial x_1} = \sum_\alpha i_\alpha^s \frac{\partial G_\alpha}{\partial x_1} + \sum_{n,\gamma} \frac{\partial p_n}{\partial x_1} \int_0^G \left( \frac{\partial i_\gamma}{\partial p_n} \right) dG_\gamma$$

The suffix  $g$  indicates differentiation at constant  $g$ . Using eq. 20-26 the calculation yields

$$\begin{aligned} \text{div}_1 \Theta &= \sum_{n=1}^{10} B_n \\ \text{where} \quad B_1 &= i_1^s \frac{\partial G_1}{\partial x_1}, \quad B_2 = G_1 \frac{\partial i_1^s}{\partial x_1}, \quad B_3 = -i_1^s \frac{\partial G_1}{\partial x_1} \\ B_4 &= -i_2^s \frac{\partial G_2}{\partial x_1}, \quad B_5 = -i_3^s \frac{\partial G_3}{\partial x_1} \\ B_6 &= -\sum_{n,\gamma} \frac{\partial p_n}{\partial x_1} \int_0^G \left( \frac{\partial i_\gamma}{\partial p_n} \right) dG_\gamma \end{aligned}$$

$$B_7 = i_2 \frac{\partial G_1}{\partial x_2}, \quad B_8 = G_1 \frac{\partial i_2}{\partial x_2}$$

$$B_9 = i_3 \frac{\partial G_1}{\partial x_3}, \quad B_{10} = G_1 \frac{\partial i_3}{\partial x_3}$$

One sees at once that

$$B_1 + B_3 = 0, \quad B_2 + B_8 + B_{10} = G_1 \operatorname{div} \mathbf{i}$$

$$B_4 + B_7 = -i_2 \operatorname{curl}_3 G, \quad B_5 + B_9 = i_3 \operatorname{curl}_2 G$$

Therefore

$$\operatorname{div} \Theta = G \operatorname{div} \mathbf{i} - [\mathbf{i} \times \operatorname{curl} G] - \sum_{n,y} \operatorname{grad} p_n \int_0^{\partial i_y} \left( \frac{\partial i_y}{\partial p_{n,y}} \right) dG_y \quad (20-27)$$

This agrees with eq. 13-5 apart from the form of the term representing inhomogeneity. The argument following eq. 13-5 in Chap. 13 does not make use of the relation between  $\mathbf{G}$  and  $\mathbf{i}$ , and therefore applies in the present case and leads to the impulse theorem (compare eq. 13-10)

$$-\operatorname{div} [T(\mathbf{E}) + T(\mathbf{H}) + \Theta] = \rho^0 \mathbf{E} + \frac{1}{c} [\mathbf{i}^0 \times \mathbf{H}] +$$

$$+ \sum_{n,y} \operatorname{grad} p_n \int_0^{\partial i_y} \left( \frac{\partial i_y}{\partial p_{n,y}} \right) dG_y + \frac{\partial}{\partial t} \left[ \frac{1}{c} [\mathbf{E} \times \mathbf{H}] + \rho^0 \mathbf{G} \right] \quad (20-28)^6$$

The whole discussion that follows the impulse theorem concerning the volume forces and the torque due to asymmetry of the tensor

$$\Theta_{23} - \Theta_{32} = [\mathbf{G} \times \mathbf{i}]_1, \text{ etc.}$$

remains valid here. The new fact that arises is that this asymmetry appears now even in cubic crystal superconductors, at least when we go beyond the region where the linear approximation is sufficient.

(g) Differences from the linear theory appear when we discuss the individual stress components. If we choose the  $x_1$  direction parallel to  $\mathbf{i}$

<sup>6</sup>From eq. 20-8 it follows by differentiation with respect to  $p_n$  at constant  $\mathbf{i}$  and  $\mathbf{G}$  that

$$\sum_y \int_0^{\partial i_y} \left( \frac{\partial i_y}{\partial p_{n,y}} \right) dG_y = - \sum_y \int_0^{\partial i_y} \left( \frac{\partial G_y}{\partial p_{n,y}} \right) di_y$$

The third term on the right-hand side of eq. 20-28 can therefore also be written in the alternative form given by M. von Laue (footnote 1)

$$- \sum_{n,y} \operatorname{grad} p_n \int_0^{\partial i_y} \left( \frac{\partial G_y}{\partial p_{n,y}} \right) di_y$$

at some point in space, four of the nine components of  $\Theta$  vanish there and the others have the values:

$$\Theta_{11} = (\mathbf{i} \cdot \mathbf{G}) - F^2, \quad \Theta_{22} = \Theta_{33} = -F^2, \quad \Theta_{21} = i_1^2 G_2, \quad \Theta_{31} = i_1^2 G_3 \quad (20-29)$$

The components  $\Theta_{11}$  and  $\Theta_{31}$  also vanish if  $\mathbf{i}$  and  $\mathbf{G}$  are parallel, and then the current line is, just as before, one of the principal axes of rotational symmetry of the tensor  $\Theta$ . A tension  $F^2$  acts perpendicular to the current line, and a pressure acts along it because  $\Theta_{22} = \Theta_{33} < 0$  while  $\Theta_{11} > 0$  according to eqs. 20-8 and 20-9. However, the pressure is no longer equal to the tension, but, by eq. 20-11 is smaller than the tension when  $\mathbf{G}$  and  $\mathbf{i}$  are related as in curve *a* of Fig. 20-1, and greater for the curve *b*.

In any case, according to eq. 20-29 a supercurrent flowing parallel to the surface of a superconductor must exert a force that has both a tangential and a normal component across the surface into the interior amounting to  $F^2$  per unit area. The work done by this field upon a surface element  $d\sigma$  displaced a distance  $\partial u$  toward the interior of the superconductor amounts therefore to  $F^2 d\sigma \partial u$ . Therefore the thermodynamic equilibrium condition at the boundary between normally and superconducting phases of the same substance is (compare Chap. 17)

$$F^2 = \frac{(f_n - f_s)}{V} \quad (20-30)$$

while at the free (outside) surface of the superconductor

$$F^2 \leq \frac{(f_n - f_s)}{V} \quad (20-31)$$

In so far as  $F^2 = \frac{1}{2} (\mathbf{i} \cdot \mathbf{G})$  this agrees with eqs. 17-3 and 17-4.

For very thick specimens we can write  $\frac{1}{2} (H^0)^2$  for  $F^2$ , by eq. 20-24 and so get exactly the form 17-6 and 17-7 for the equilibrium conditions. As the whole of the thermodynamics of this transition can be derived from this condition, according to Chap. 17, it remains unaffected by altering the electrostatics in the above manner. For a plate of finite thickness however  $C > 0$  in eq. 20-18 by section (c). If the magnetic field on both sides of the plate has the critical value  $H_c$ , then by eq. 20-31,  $F^2$  at the boundary has a lower value than the critical one. We then have to increase the external field to bring  $F^2$  to its critical value, i. e., for thin superconductors the critical field strength is greater than for thick ones. This agrees qualitatively with the results of Chap. 18, which however no longer hold quantitatively in the nonlinear theory. The results depend on the relation between  $\mathbf{G}$  and  $\mathbf{i}$  so that it should in principle be possible to derive conclusions about this relation from experimental data on the dependency of the critical magnetic field on the thickness of the plate.

(h) We now turn to the case where there does exist a maximum current density  $i_m$ , i. e., the family of surfaces in  $\mathbf{i}$  space converge upon a finite surface on which  $F^2$  becomes infinite.

We consider first the superconductor of section (c), occupying half of space. If  $i_1^2$  at the surface is only a little below  $i_m^2$ , while  $i_2^2 = 0$  (this can

always be done by choosing the appropriate direction for the coordinates  $x_1$  and  $x_2$ , then by eq. 20-15  $G_1$  decreases with increasing  $x_3$ , but not as in Chap. 7 (exponentially in one way or another) but much more slowly, approximately in the form of a parabola. By eq. 20-13  $H_2$  thus becomes a linear function of  $x_3$  (compare Fig. 20-2), and this causes the protecting layer to become thicker than on the linear theory. As a matter of fact, to completely shield the field  $H^0$  the Maxwell theory would require a total surface current  $cH^0$ , and this, when the current density is limited, would have to be distributed over a thicker protecting layer. The penetration depth therefore becomes greater than in the linear theory and dependent on  $H^0$ .

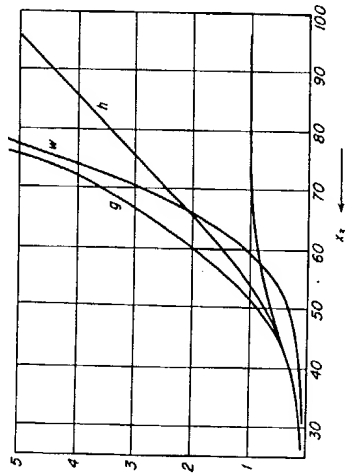


Fig. 20-2. Field distribution in the superconductor filling half space  $x_3 > 0$  according to Koppe (see footnote 1, Chapter 20). Abscissa:  $x_3$  in units of  $\exp \sqrt{\lambda}$ . Ordinate:

$$i = |H|/i_m, \quad h = H/\sqrt{\lambda} i_m \\ g = G/c\sqrt{\lambda} i_m, \quad w = F/\lambda i_m^2$$

When a cylinder of radius  $R$  (section  $d$ ) carries a current, the field  $H^0$  at the surface is definitely less than the value  $R i_m/2c$  that would exist if the current density were equal to  $i_m$  over the whole cross section. In spite of this limitation on  $H^0$ ,  $F$  can by eq. 20-23 attain any value at the surface, including the critical value given by eq. 20-31, so long as  $F_0$  already has approximately this value, i. e., so long as the current is somewhat uniformly distributed over the cross section.<sup>7</sup> But  $F_0$  is nowhere so great as it is at the surface, and it is there that the greatest danger to the superconductivity lies, and it is also there that the breakdown starts as soon as  $F_0$  reaches the critical value. This is true no matter how great the critical value may

<sup>7</sup>The same conclusion can be drawn from eq. 20-18 with  $C < 0$ .

be or how small the maximum current density. The upper limit of the current density is therefore not a new condition for the stability of the supercurrent; the thermodynamic relations 20-30 or 20-31 are still necessary and sufficient.<sup>8</sup>

(i) Although the nonlinear theory agrees at least qualitatively, and in many important problems even quantitatively, with the linear theory for all stationary fields, in discussing oscillatory fields the linear theory can only be regarded as an approximation for oscillations of sufficiently small amplitude.

### Proof of Equation 14-8

If matter undergoes an arbitrary but continuous displacement  $\partial u$  then the change  $dP$  of an arbitrary vector  $P$  at a moving (material) point is related with the change  $\partial P$  at a given point in space through the equation

$$dP_a = \partial P_a + \sum_y \partial u_y \frac{\partial P_a}{\partial x_y} + \frac{1}{2} [P \times \text{curl } \partial u]_a$$

Therefore

$$d(P_a P_\beta) = \partial(P_a P_\beta) + P_\alpha \left\{ \sum_y \partial u_y \frac{\partial P_\beta}{\partial x_y} + \frac{1}{2} [P \times \text{curl } \partial u]_\beta \right\} \\ + P_\beta \left\{ \sum_y \partial u_y \frac{\partial P_\alpha}{\partial x_y} + \frac{1}{2} [P \times \text{curl } \partial u]_\alpha \right\} \quad (a)$$

$P_\alpha P_\beta$  are the components of a symmetrical tensor, say  $t_{\alpha\beta}$ . For the most general formulation of the symmetrical tensor we have to combine three noncoplanar vectors  $P$ ,  $Q$ ,  $R$  as follows:

$$P_\alpha P_\beta + Q_\alpha Q_\beta + R_\alpha R_\beta$$

The two additional terms do not alter the form of the transformation of  $d t_{\alpha\beta}$  into  $\partial t_{\alpha\beta}$ , so we confine ourselves to the definition

$$t_{\alpha\beta} = P_\alpha P_\beta$$

Transcribing (a) we then have

$$d t_{11} = \partial t_{11} + \sum_y \partial u_y \frac{\partial t_{11}}{\partial x_y} + \frac{1}{2} (t_{12} \text{curl}_3 \partial u - t_{13} \text{curl}_2 \partial u)$$

<sup>8</sup>According to the above considerations (see M. von Laue, footnote 1), Silsbee's hypothesis [compare Chap. 1 (e)] is now valid only for sufficiently "thick" superconductors.

$$\partial t_{23} = \partial t_{23} + \sum_y \partial u_y \frac{\partial t_{23}}{\partial x_y} + \frac{1}{2} \{ (t_{33} - t_{22}) \text{curl}_1 \partial u + t_{12} \text{curl}_2 \partial u - t_{13} \text{curl}_3 \partial u \}$$

etc.

Just as in Chap. 14 we now assume that all the  $\partial t_{\alpha\beta}$ 's are zero so that

$$\partial t_{11} = - \sum_y \partial u_y \frac{\partial t_{11}}{\partial x_y} - \frac{1}{2} (t_{13} \text{curl}_2 \partial u - t_{12} \text{curl}_3 \partial u) \quad (b)$$

$$\partial t_{23} = - \sum_y \partial u_y \frac{\partial t_{23}}{\partial x_y} + \frac{1}{2} \{ (t_{22} - t_{33}) \text{curl}_1 \partial u - t_{12} \text{curl}_2 \partial u + t_{13} \text{curl}_3 \partial u \}$$

Let  $\mathbf{Q}$  be another arbitrary vector. In (b) collect all the terms with  $\text{curl}_1 \partial u$ , all those with  $\text{curl}_2 \partial u$  and all those with  $\text{curl}_3 \partial u$ , and obtain

$$\begin{aligned} \frac{1}{2} \sum_{\alpha\beta} Q_\alpha Q_\beta \partial t_{\alpha\beta} &= \frac{1}{2} Q_1^2 \partial t_{11} + \dots + Q_3 Q_3 \partial t_{33} + \dots = \\ &- \frac{1}{2} \sum_{\alpha\beta\gamma} Q_\alpha Q_\beta \frac{\partial t_{\alpha\beta}}{\partial x_\gamma} \partial u_\gamma \\ &+ \frac{1}{2} \{ \text{curl}_1 \partial u [(Q_3^2 - Q_2^2) \partial t_{23} + Q_1 Q_3 t_{12} - Q_1 Q_2 t_{13} + Q_3 Q_3 (t_{22} - t_{33})] \\ &+ \text{curl}_2 \partial u [\text{a similar factor to the above}] \\ &+ \text{curl}_3 \partial u [\text{a similar factor to the above}] \} \end{aligned}$$

This equation can be simplified by introducing the following vector:

$$\mathbf{R}_\alpha \equiv \sum_\beta t_{\alpha\beta} Q_\beta$$

We then obtain

$$\frac{1}{2} \sum_{\alpha\beta} Q_\alpha Q_\beta \partial t_{\alpha\beta} = - \frac{1}{2} \sum_{\alpha\beta} Q_\alpha Q_\beta (\partial u \cdot \nabla t_{\alpha\beta}) + \frac{1}{2} (\text{curl} \partial u \cdot [\mathbf{R} \times \mathbf{Q}]) \quad (c)$$

Finally writing  $\mathbf{r}$  in place of  $\mathbf{Q}$ ,  $\mathbf{G}$  for  $\mathbf{R}$  and  $\lambda_{\alpha\beta}$  for  $t_{\alpha\beta}$  we confirm eq. 14-8.

## INDEX

- Acceleration theory, 18
- Bessel equation, 35
- functions, 36
- Cathode rays, 19, 20
- Crystals, and superconduction, 15-17
- Debye's law, 110
- Eddy currents, 102
- Electrons mean free path, 102, 103
- Energy, 20-22
- electric, 9
- free, 22, 104; 106
- density, 127-137
- temperature dependence, 106
- magnetic, 9
- total density, 21
- Entropy, 106, 107
- Equilibrium conditions, 105, 109
- stable, 71
- Extinction coefficient, 92
- Hankel function, 44
- Induction, coefficient, 12, 14
- equations, 9, 11
- Kirchhoff's rule 8, 9
- Lattice structure 4
- and conducting phase, 103
- Lines of force, for sphere, 60
- thin cylinder, 52
- London's fundamental equations, 14
- relativistic form, 14
- London stresses, 75-84, 118
- and torque, 82
- surface divergence, 18
- tension, 104
- Magnetic field
- critical value, 4, 6, 105, 112, 120, 126
- at transition temperature, 108
- temperature dependence, 5, 108
- thin superconductors, 27, 112-120, 135
- distortion, 7, 112
- circular cylinder, 55
- sphere, 58
- external, penetration of, 121
- in superconductors, 6-8, 30
- intensification factor, 112
- moment, 70
- Maxwell equations, 13
- from least action principle, 9, 10
- Maxwell-London theory, 12
- Maxwell stresses, 75-84
- and torque, 82, 84
- tensors of, 77
- Maxwell theory, 6
- Meissner effect, 7, 27, 30, 66, 80, 106, 129-132
- and skin effect, 94
- superconducting states, 107
- disappearance of, 121
- Momentum law, equation of, 78
- Multiply connected region, 62
- Nernst theorem, 106, 108
- Ohmic current, 106
- distribution in superconductor, 72
- existence of, 94
- Penetration depth, 3, 126
- and alternating currents, 94-103
- mean free path of electrons, 102, 103
- non-linear theory, 136
- of magnetic field, 27
- increase, 67



- Penetration near transition temperature, 32  
 — relation to flux of induction, 75  
 Persistent current, 3, 10, 61—75, 132  
 — energy, 73, 74, 91  
 — in doubly connected body, 41, 49  
 — — ring, 68  
 — production, 70  
 Potential, scalar and vector, 61  
 — superconduction 63  
 — — period of, 65, 67, 85  
 Poynting sector, 21, 78, 96  
 Refractive index, 92, 93  
 Silsbee hypothesis, 6, 118  
 Skin effect, 94—103  
 Specific heat, 107, 108  
 — of conduction electrons, 110  
 — at transition temperature, 110  
 Stress tensor, 76  
 — and non-linear theory, 133  
 Superconductivity  
 — atomic theory, 126  
 — breakdown, 105, 126  
 — quenching, 7, 8, 112  
 — — for thin specimen, 113  
 — — — sphere, 121  
 — permanent magnetism, 89, 106  
 Superconductor, crystal systems, 2  
 — current distribution, 11  
 — displacement of current lines 72  
 Superconductor field free state, 7, 103  
 — homogeneous cubic, 26  
 — inhomogeneous, 88  
 — magnetic field, 4, 12  
 — space charges, 19, 20, 128  
 — thin—27—34  
 Super current 3, 4  
 — critical value of 6, 114, 115  
 — in circular cylinder, 35  
 — — elliptic cylinder, 53  
 — — hollow cylinder, 44  
 — — stationary field, 68  
 — maximum density, 126—137  
 — stability of 75, 76  
 — velocity of 83, 84  
 Supermomentum, 78  
 Thermal expansion coefficient, 4  
 Thermodynamics, 7, 103—112  
 — equilibrium, 105, 119  
 Transition from normal to superconductivity, 4  
 — magnetic effect, 13  
 Transition temperature  
 — and magnetic field, 108  
 — — penetration depth, 32  
 — — resistance, 1, 2  
 — — specific heat, 110  
 — of metals, 2  
 Uniqueness theorem, 25, 68

# Attachment B

The Research Libraries of The New York Public Library / All Locations - Netscape

Forward Stop

http://catnyp.nypl.org/search/q

**CATNYP: The Online Catalog of The New York Public Library**  
The Research Libraries

ANOTHER SEARCH START OVER EXPORT

You searched:   in

Limited to: Words in the TITLE "new directions in s"

Call # JSD 88-446

Author Rao, C. N. R. (Chintamani Nagesa Ramachandra), 1934-

Title **New directions in solid state chemistry : structure, synthesis, properties, reactions**  
**Rao, J. Gopalakrishnan.**

Imprint Cambridge [Cambridgeshire] ; New York : Cambridge University Press, 1986.

LOCATION	CALL #
Science & Business Lib	JSD 88-446

Location Science & Business Lib

Descript x, 516 p. : ill. ; 23 cm.

Series Cambridge solid state science series

Note Includes index.  
Bibliography: p. [475]-503.

Subject Solid state chemistry.

Add'l name Gopalakrishnan, J. (Jagannatha), 1939-

ANOTHER SEARCH START OVER EXPORT

**CATNYP: The Online Catalog of The New York Public Library**

Daniel P. Morris, Ph.D.  
Staff Counsel  
IBM Research  
IP Law Department Yorktown  
Tie line: 8-862-3217  
Phone: 914-945-3217  
Fax: 914-945-3281

# Attachment C

# Synthesis of cuprate superconductors\*

C N R Rao, R Nagarajan and R Vijayaraghavan

Solid State and Structural Chemistry Unit and CSIR Centre of Excellence in Chemistry, Indian Institute of Science, Bangalore 560012, India

Received 28 August 1992, in final form 19 October 1992

**Abstract.** There has been unprecedented activity pertaining to the synthesis and characterization of superconducting cuprates in the last few years. A variety of synthetic strategies has been employed to prepare pure monophasic cuprates of different families with good superconducting properties. Besides the traditional ceramic method, other methods such as coprecipitation and precursor methods, the sol-gel method, the alkali flux method and the combustion method have been employed for the synthesis of cuprates. Depending on the requirements, varying conditions such as high oxygen or hydrostatic pressure and low oxygen fugacity are employed in the synthesis. In this review, we discuss the synthesis of the various types of cuprate superconductors and point out the advantages and disadvantages of the different methods. We have provided the necessary preparative details, presenting the crucial information in tabular form wherever necessary.

## 1. Introduction

Since the discovery of high- $T_c$  superconductivity in the La-Ba-Cu-O system [1], a variety of cuprate superconductors with  $T_c$ s going up to 128 K have been synthesized and characterized [2, 3]. No other class of materials has been worked on so widely and intensely in recent years as have the cuprate superconductors. Several methods of synthesis have been employed for preparing the cuprates, with the objective of obtaining pure monophasic products with good superconducting characteristics [3, 4]. The most common method of synthesis of cuprate superconductors is the traditional ceramic method which has been employed for the preparation of a large variety of oxide materials [5]. Although the ceramic method has yielded many of the cuprates with satisfactory characteristics, different synthetic strategies have become necessary in order to control factors such as the cation composition, oxygen stoichiometry, cation oxidation states and carrier concentration. Specially noteworthy amongst these methods are chemical or solution routes which permit better mixing of the constituent cations in order to reduce the diffusion distances in the solid state [5, 6]. Such methods include coprecipitation, use of precursors, the sol-gel method and the use of alkali fluxes. The combustion method or self-propagating high-temperature synthesis (SHS) has also been employed. In this review, we will discuss the preparation of cuprate superconductors by the different methods, mentioning

the special features of each method and the conditions employed for the synthesis. In table 1, we give a list of the cuprate superconductors discussed in this review along with their structural parameters and approximate  $T_c$  values. Preparative conditions such as reaction temperature, oxygen pressure, hydrostatic pressure and annealing conditions are specified in the discussion and given in tabular form where necessary. It is hoped that this review will be found useful by practitioners of the subject as well as those freshly embarking on the synthesis of these materials.

## 2. Ceramic method

The most common method of synthesizing inorganic solids is by the reaction of the component materials at elevated temperatures. If all the components are solids, the method is called the ceramic method [5]. If one of the constituents is volatile or sensitive to the atmosphere, the reaction is carried out in sealed evacuated capsules. Platinum, silica or alumina containers are generally used for the synthesis of metal oxides. The starting materials are metal oxides, carbonates, or other salts, which are mixed, homogenized and heated at a given temperature sufficiently long for the reaction to be completed. A knowledge of the phase diagram is useful in fixing the composition and conditions in such a synthesis.

The ceramic method generally requires relatively high temperatures (up to 2300 K) which are generally attained by resistance heating. Electric arc and skull

\* Contribution No 874 from the Solid State and Structural Chemistry Unit.

**Table 1.** Structural parameters and approximate  $T_c$  values of cuprate superconductors.

Cuprate	Structure	$T_c$ (K) (max. value)
1 $\text{La}_2\text{CuO}_{4+x}$	Bmab; $a = 5.355$ , $b = 5.401$ , $c = 13.15$ Å	39
2 $\text{La}_{2-x}\text{Sr}_x(\text{Ba})\text{CuO}_4$	I4/mmm; $a = 3.779$ , $c = 13.23$ Å	35
3 $\text{La}_2\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_2\text{O}_6$	I4/mmm; $a = 3.825$ , $c = 19.42$ Å	60
4 $\text{YBa}_2\text{Cu}_3\text{O}_7$	Pmmm; $a = 3.821$ , $b = 3.885$ , $c = 11.676$ Å	93
5 $\text{YBa}_2\text{Cu}_4\text{O}_8$	Ammm; $a = 3.84$ , $b = 3.87$ , $c = 27.24$ Å	80
6 $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$	Ammm; $a = 3.851$ , $b = 3.869$ , $c = 50.29$ Å	93
7 $\text{Bi}_2\text{Sr}_2\text{CuO}_6$	Amaa; $a = 5.362$ , $b = 5.374$ , $c = 24.622$ Å	10
8 $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$	A2aa; $a = 5.409$ , $b = 5.420$ , $c = 30.93$ Å	92
9 $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}$	A2aa; $a \sim 5.39$ , $b \sim 5.40$ , $c \sim 37$ Å	110
10 $\text{Bi}_2\text{Sr}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_{10}$	P4/mmm; $a = 3.888$ , $c = 17.28$ Å	25
11 $\text{Tl}_2\text{Ba}_2\text{CuO}_6$	A2aa; $a = 5.468$ , $b = 5.472$ , $c = 23.238$ Å; I4/mmm; $a = 3.866$ , $c = 23.239$ Å	92
12 $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$	I4/mmm; $a = 3.855$ , $c = 29.318$ Å	119
13 $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$	I4/mmm; $a = 3.85$ , $c = 35.9$ Å	128
14 $\text{Tl}(\text{BaLa})\text{CuO}_5$	P4/mmm; $a = 3.83$ , $c = 9.55$ Å	40
15 $\text{Tl}(\text{SrLa})\text{CuO}_5$	P4/mmm; $a \sim 3.7$ , $c \sim 9$ Å	40
16 $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{CuO}_5$	P4/mmm; $a = 3.738$ , $c = 9.01$ Å	40
17 $\text{TlCaBa}_2\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.856$ , $c = 12.754$ Å	103
18 $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{CaSr}_2\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.80$ , $c = 12.05$ Å	90
19 $\text{TlSr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.80$ , $c = 12.10$ Å	90
20 $\text{TlCa}_2\text{Ba}_2\text{Cu}_3\text{O}_8$	P4/mmm; $a = 3.853$ , $c' = 15.913$ Å	110
21 $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$	P4/mmm; $a = 3.81$ , $c = 15.23$ Å	120
22 $\text{TlBa}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_9$	I4/mmm; $a \sim 3.8$ , $c \sim 29.5$ Å	40
23 $\text{Pb}_2\text{Sr}_2\text{Ln}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_8$	Cmmm; $a = 5.435$ , $b = 5.463$ , $c = 15.817$ Å	70
24 $\text{Pb}_2(\text{Sr}, \text{La})_2\text{Cu}_2\text{O}_6$	P22 <sub>1</sub> 2; $a = 5.333$ , $b = 5.421$ , $c = 12.609$ Å	32
25 $(\text{Pb}, \text{Cu})\text{Sr}_2(\text{Ln}, \text{Ca})\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.820$ , $c = 11.826$ Å	50
26 $(\text{Pb}, \text{Cu})(\text{Sr}, \text{Eu})(\text{Eu}, \text{Ce})\text{Cu}_2\text{O}_8$	I4/mmm; $a = 3.837$ , $c = 29.01$ Å	25
27 $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$	I4/mmm; $a = 3.95$ , $c = 12.07$ Å	30
28 $\text{Ca}_{1-x}\text{Sr}_x\text{CuO}_2$	P4/mmm; $a = 3.902$ , $c = 3.35$ Å	110
29 $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$	P4/mmm; $a = 3.942$ , $c = 3.393$ Å	40

techniques give temperatures up to 3300 K while high-power  $\text{CO}_2$  lasers give temperatures up to 4300 K. The main disadvantages of the ceramic method are the following:

(i) The starting mixtures are inhomogeneous at the atomic level.

(ii) When no melt is formed during the reaction, the entire reaction has to occur in the solid state, first by a phase boundary reaction at the points of contact between the components and later by the diffusion of the constituents through the product phase. With the progress of the reaction, diffusion paths become longer and the reaction rate slower; the reaction can be speeded up to some extent by intermittent grinding between heating cycles.

(iii) There is no simple way of monitoring the progress of the reaction. It is by trial and error that one decides on the appropriate conditions required for the completion of the reaction. Because of this difficulty, with the ceramic method one often ends up with mixtures of reactants and products. Separation of the desired products from such mixtures is difficult, if not impossible.

(iv) Frequently it becomes difficult to obtain a compositionally homogeneous product even where the reaction proceeds nearly to completion.

Despite the above limitations, the ceramic method is widely used for the synthesis of a large variety of inorganic solids. In the case of the cuprate superconductors,

the ceramic method involves mixing and grinding the component oxides, carbonates or other salts, and heating the mixture, generally in pellet form, at the desired temperature. A common variation of the method is to heat a mixture of nitrates obtained by digesting the metal oxides/carbonates in concentrated  $\text{HNO}_3$  and evaporating the solution to dryness. Heating is carried out in air or in an appropriate atmosphere, controlling the partial pressure of oxygen where necessary. In the case of thallium cuprates, because of the volatility and poisonous nature of the thallium oxide vapour, reactions are carried out in sealed tubes. In some of the earlier preparations, the thallium cuprates were synthesized in open furnaces. This is however, not recommended. A successful synthesis by the ceramic method depends on several factors which include the nature of the starting materials (the choice of oxides, carbonates), the homogeneity of the mixture of powders, the rate of heating as well as the reaction temperature and duration.

## 2.1. $\text{La}_2\text{CuO}_4$ -related 214 cuprates

Synthesis of alkaline-earth-doped  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  ( $\text{M} = \text{Ca}, \text{Sr}$  and  $\text{Ba}$ ) of  $\text{K}_2\text{NiF}_4$  structure with superconducting transition temperatures up to 35 K is readily achieved by the ceramic method. Typically, the synthesis is carried out by reacting stoichiometric quantities of the oxides and/or carbonates around 1300 K in

air [1-9]. A few groups have annealed the samples in an oxygen atmosphere at 673 K after the sintering step [10]. Metal nitrates have also been used as the starting materials for the synthesis [11-13]. By starting with metal nitrates, one obtains a more homogeneous starting mixture, since the hydrated metal nitrates have low melting points leading to a uniform melt in the initial stage of the reaction. Furthermore, nitrates provide an oxidative atmosphere, which is required to obtain the necessary oxygen content.

Stoichiometric  $\text{La}_2\text{CuO}_4$  is an antiferromagnetic insulator.  $\text{La}_2\text{CuO}_4$  prepared under high oxygen pressures, however, shows superconductivity ( $T_c \sim 35$  K) since the oxygen excess introduces holes just as the alkaline earth dopants [14-16].  $\text{La}_2\text{CuO}_{4+\delta}$  ( $\delta$  up to 0.05) has been synthesized by annealing  $\text{La}_2\text{CuO}_4$  under an oxygen pressure of 3 kbar at 870 K [14, 15] or 23 kbar at 1070 K [16]. Oxygen plasma has also been used to increase the oxygen content.

The next homologue of  $\text{La}_2\text{CuO}_4$  containing two Cu-O layers,  $\text{La}_{1.6}\text{Sr}_{0.4}\text{CaCu}_2\text{O}_6$  ( $T_c \sim 60$  K), has been synthesized by using high oxygen pressures [17]. The synthesis involves heating the sample at an oxygen pressure of around 20 bar at 1240 K. The material prepared at ambient oxygen pressures (in air) is an insulator. Several other high-oxygen-pressure preparations have been reported on the  $n=2$  member of the  $\text{La}_{n+1}\text{Cu}_n\text{O}_{2n+3}$  homologous series by making use of commercially available high-pressure furnaces [18, 19]. In table 2, we have summarized the preparative conditions for 123 and related cuprate superconductors.

## 2.2. $\text{YBa}_2\text{Cu}_3\text{O}_7$ and other 123 cuprates

Superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  with the orthorhombic structure can be easily prepared by the ceramic method. Most of the investigations of the 123 compound,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  have been carried out on the materials prepared by reacting  $\text{Y}_2\text{O}_3$  and  $\text{CuO}$  with  $\text{BaCO}_3$  [20, 21]. It is noteworthy that Rao *et al* [21] obtained monophasic  $\text{YBa}_2\text{Cu}_3\text{O}_7$  as the  $x=1.0$  member of the  $\text{Y}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14}$  series. In the method employed for preparing  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , stoichiometric quantities of high-purity  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{CuO}$  are ground thoroughly and heated initially in powder form around 1223 K for a period of 24 h. Following the calcination step, the powder is ground, pelletized and sintered at the same temperature for another 24 h. Finally, annealing is carried out in an atmosphere of oxygen around 773 K for 24 h to obtain the orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  phase showing 90 K superconductivity. Oxygen annealing has to be carried out below the orthorhombic tetragonal transition temperature ( $\sim 960$  K); tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $0.6 \leq \delta \leq 1.0$ ) is not superconducting. Intermittent grinding is necessary to obtain monophasic, homogeneous powders. This kind of complex heating schedule often gives rise to microscopic compositional inhomogeneities. Furthermore,  $\text{CO}_2$  released from the decomposition of  $\text{BaCO}_3$  can react with  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  to form non-superconducting

phases at the grain boundaries. One way of avoiding the evolution of  $\text{CO}_2$  during the synthesis is to use  $\text{BaO}_2$  instead of  $\text{BaCO}_3$  [22, 23]. Some of the impurities or side products in the preparation of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  are  $\text{BaCuO}_2$ ,  $\text{Y}_2\text{BaCuO}_5$  and  $\text{Y}_2\text{Cu}_2\text{O}_5$  [24]. The ternary phase diagram given in figure 1 illustrates the complexities of this cuprate system.

Using  $\text{BaO}_2$  as the starting material has two advantages. It has a lower decomposition temperature than  $\text{BaCO}_3$  and the 123 compound is therefore formed at relatively low temperatures.  $\text{BaO}_2$  acts as an internal oxygen source and the duration of annealing in an oxygen atmosphere is reduced to a considerable extent. Sharp superconducting transitions are observed in samples of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  made using  $\text{BaO}_2$ . Slight excess of copper in the ceramic method is reported to give cuprates with sharper transitions [25]. Preparation of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is accomplished in a shorter period if one employs metal nitrates as the starting materials [13, 23]. In table 2, we present the conditions employed for preparing 123 cuprates by the ceramic method.

Other rare-earth cuprates of the 123 type,  $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$  where  $\text{Ln} = \text{La, Nd, Sm, Eu, Gd, Dy, Ho, Er}$  and  $\text{Tm}$  (all with  $T_c$  values around 90 K) have also been prepared by the ceramic method [26, 27]. Oxygen annealing of these cuprates should also be carried out below the orthorhombic-tetragonal transition temperature [3]: La, 754 K; Nd, 837 K; Gd, 915 K; Er, 973 K; Yb, 976 K etc. Nearly 30% of Y can be substituted by Ca in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , retaining the basic crystal structure [28]; the  $T_c$  decreases with the increase in calcium content. Both La and Sr can be substituted at the Ba site in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  [29-31]. With La, monophasic products are obtained for  $0 \leq x \leq 1.0$  in  $\text{YBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7-\delta}$ , the  $T_c$  decreasing with increase in  $x$ . In the case of Sr substitution, monophasic products are obtained for  $0 \leq x \leq 1.25$  in  $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-\delta}$ ; high  $T_c$  is retained up to  $x=1.0$ . Ceramic methods have also been used to prepare  $\text{YBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-\delta}$  solid solutions, where M generally stands for a transition element of the first series. In most

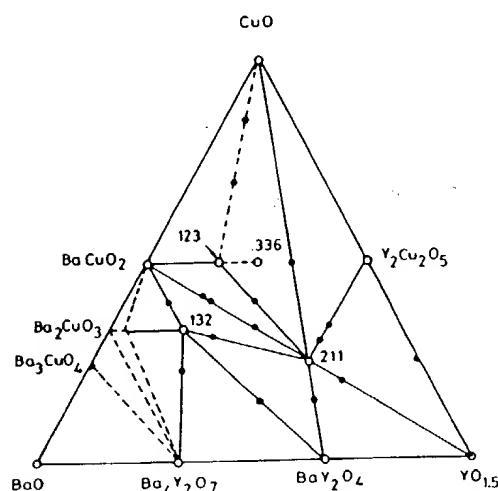


Figure 1. Phase diagram of the  $\text{Y}_2\text{O}_3$ -BaO-CuO system at 1220 K (from [24]).

Table 2. Preparative conditions for the synthesis of 214, 123, 124 and 247 type cuprates by the ceramic method.

Compound	Starting materials	Preparative conditions			Comments	$T_c$ (K)	Ref.
		Temp. (K)	Time	Gas			
$\text{La}_2\text{CuO}_{4+x}$	$\text{La}_2\text{O}_3 \cdot \text{CuO}$	1273 873	24 h 12–48 h	air $\text{O}_2$	3 kbar pressure	35	[15]
$\text{La}_{2-x}\text{Sr}_x(\text{Ba}_y)\text{CuO}_4$	$\text{La}_2\text{O}_3 \cdot \text{Sr}/\text{BaCO}_3 \cdot \text{CuO}$	1393	36 h	$\text{O}_2$		40	[10]
$\text{La}_{1.8}\text{Sr}_{0.2}\text{CaCu}_2\text{O}_6$	$\text{La}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O} \cdot \text{Sr}/\text{Ba}(\text{NO}_3)_2 \cdot \text{Cu}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$	1273	20 h	air		32	[13]
	$\text{La}_2\text{C}_2\text{O}_4 \cdot 10\text{H}_2\text{O} \cdot \text{Sr}(\text{NO}_3)_2 \cdot \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} \cdot \text{CuO}$	973	16 h	$\text{O}_2$			
		1173	3 d	$\text{O}_2$			
		1198	3 d	$\text{O}_2$			
$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ <sup>a</sup>	$\text{Y}_2\text{O}_3 \cdot \text{BaCO}_3 \cdot \text{CuO}$	1243	2 d	$\text{O}_2$	20 atm	60	[17]
		1223	2 d	air		88	[20]
	$\text{Y}_2\text{O}_3 \cdot \text{BaO}_2 \cdot \text{CuO}$	773	1 d	$\text{O}_2$		89	[22]
		723	1 d	$\text{O}_2$		90	[13]
$\text{YBa}_2\text{Cu}_4\text{O}_8$ <sup>b</sup>	$\text{Y}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O} \cdot \text{Ba}(\text{NO}_3)_2 \cdot \text{Cu}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$	1173	16 h	air		81	[34]
		1223	1 h	$\text{O}_2$		77	[35]
	$\text{Y}_2\text{O}_3 \cdot \text{BaCO}_3 \cdot \text{CuO}$	1313	—	$\text{O}_2$	400 bar	78	[36, 38]
	$\text{Y}_2\text{O}_3 \cdot \text{Ba}(\text{NO}_3)_2 \cdot \text{CuO} + \text{equal volumes of Na}_2\text{CO}_3 \text{ or K}_2\text{CO}_3$	1023	1 d	$\text{O}_2$	124 major phase + BaCuO <sub>2</sub> impurity		
	$\text{Y}_2\text{O}_3 \cdot \text{Ba}(\text{NO}_3)_2 \cdot \text{CuO} + 0.2\text{M NaNO}_3 \text{ or KNO}_3 \text{ or Na}_2\text{O}_2$	1073	3 d	$\text{O}_2$	124 major phase + BaCuO <sub>2</sub> + Y <sub>2</sub> BaCuO <sub>5</sub>		
		1073	3 d	$\text{O}_2$	124 major phase + BaCuO <sub>2</sub> + Y <sub>2</sub> BaCuO <sub>5</sub>		
	$\text{Y}_2\text{O}_3 \cdot \text{BaCuO}_2 \cdot \text{CuO}$	1073	1 d	air	124 major phase + BaCuO <sub>2</sub> + Y <sub>2</sub> BaCuO <sub>5</sub>	78	[36]
	$\text{Y}_2\text{O}_3 \cdot \text{BaCuO}_2 \cdot \text{CuO} + 0.2\text{M NaNO}_3 + 10 \text{ drops of dilute HNO}_3$	1088	2 d	$\text{O}_2$	124 single phase	79	[40]
$\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ <sup>c</sup>	$\text{YBa}_2\text{Cu}_3\text{O}_7 \cdot \text{CuO}$	1088	3 d	$\text{O}_2$	124 major phase + BaCuO <sub>2</sub>	75	[39]
	$\text{Y}_2\text{O}_3 \cdot \text{BaCO}_3 \cdot \text{CuO}$	1203	8 h	$\text{O}_2$	19 bar	90	[50]
	$\text{Y}_2\text{O}_3 \cdot \text{Ba}(\text{NO}_3)_2 \cdot \text{CuO}$	1133	5 d	$\text{O}_2$	Single phase	90	[36]
	$\text{Y}_2\text{O}_3 \cdot \text{Ba}(\text{NO}_3)_2 \cdot \text{CuO} + 0.2\text{M NaNO}_3$	1133	4 d	$\text{O}_2$	Single phase	90	[36]

<sup>a</sup> Other rare-earth derivatives of the type  $\text{LnBa}_2\text{Cu}_3\text{O}_7$  are also prepared by this method. Oxygen annealing is carried out below the orthorhombic-tetragonal transition temperature [26, 27].

<sup>b</sup> Other rare-earth derivatives of the type  $\text{LnBa}_2\text{Cu}_4\text{O}_8$  are obtained by a similar procedure [36, 40].

<sup>c</sup> Other rare-earth derivatives of the type  $\text{Ln}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$  are prepared by a similar procedure [36, 38].



such substituted derivatives, the  $T_c$  increases quite rapidly with increasing level of substitution [32, 33].

### 2.3. $\text{YBa}_2\text{Cu}_4\text{O}_8$ (124), $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ (247) and related cuprates

The first bulk synthesis of  $\text{YBa}_2\text{Cu}_4\text{O}_8$  was reported by Karpinski *et al* [34] who heated the mixture of oxides at 1313 K, under an oxygen pressure of 400 bar. Synthesis of  $\text{YBa}_2\text{Cu}_4\text{O}_8$  by the conventional ceramic method without the use of high oxygen pressure suffered from some limitations due to kinetic factors. Cava *et al* [35] found that additives such as alkali carbonates enhance the reaction rate. The procedure involves two steps. In the first step  $\text{Y}_2\text{O}_3$ ,  $\text{Ba}(\text{NO}_3)_2$  and  $\text{CuO}$  are mixed in the stoichiometric ratio and heated at 1023 K for 16–24 h in an oxygen atmosphere. In the second step, the pre-reacted powder is ground with an approximately equal volume of either  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$  powder and pellets of the resulting mixture are heated at 1073 K in flowing oxygen for 3 days. After the reaction, the product is washed with water to remove the excess alkali carbonate and dried by gentle heating in air. The product after this step has  $\text{YBa}_2\text{Cu}_4\text{O}_8$  as the majority phase ( $T_c$ , 77 K) with little  $\text{BaCuO}_2$  impurity. Other reaction rate enhancers such as  $\text{NaNO}_3$ ,  $\text{KNO}_3$ , dilute  $\text{HNO}_3$  and  $\text{Na}_2\text{O}_2$  have also been used successfully (in small quantities) to prepare  $\text{YBa}_2\text{Cu}_4\text{O}_8$  [36–38]. The 124 cuprate can also be prepared without the addition of a rate enhancer by the solid state reaction of  $\text{Y}_2\text{O}_3$ ,  $\text{BaCuO}_2$  and  $\text{CuO}$  at 1088 K in flowing oxygen [36]. Synthesis of  $\text{YBa}_2\text{Cu}_4\text{O}_8$  from the solid state reaction between  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{CuO}$  in flowing oxygen has also been reported [39]. The synthesis of  $\text{YBa}_2\text{Cu}_4\text{O}_8$  by the ceramic method generally takes a long time and requires repeated grinding and pelletizing.

Other rare-earth 124 cuprates,  $\text{LnBa}_2\text{Cu}_4\text{O}_8$  with  $\text{Ln} = \text{Eu, Gd, Dy, Ho}$  and  $\text{Er}$  have been prepared by the ceramic method under an oxygen pressure of 1 atm [36, 40]. The  $T_c$  of these cuprates decreases with the increasing ionic radius of the rare earth. Calcium can be substituted at the Y site up to 10% in  $\text{YBa}_2\text{Cu}_4\text{O}_8$ , and the  $T_c$  increases from 79 K to 87 K in such substituted  $\text{YBa}_2\text{Cu}_4\text{O}_8$  [41]. Lanthanum can be substituted for barium in  $\text{YBa}_2\text{Cu}_4\text{O}_8$  [42]. Single phases of  $\text{YBa}_{2-x}\text{La}_x\text{Cu}_4\text{O}_8$  have been obtained for  $0 \leq x \leq 0.4$  with the  $T_c$  decreasing with increase in  $x$ .

Extensive studies have been carried out on the synthesis of  $\text{YBa}_2\text{Cu}_4\text{O}_8$  under high oxygen pressures [43, 44]. The  $P$ - $T$  phase diagram of 124, 123 and 247 cuprates is shown in figure 2. High-oxygen pressure synthesis essentially involves the solid state reaction followed by sintering under high oxygen pressures. The typical sintering temperature and the pressure at which synthesis of  $\text{YBa}_2\text{Cu}_4\text{O}_8$  has been carried out are 1200 K and 120 atm of oxygen (for 8 h). By the use of high oxygen pressures [45], it is possible to prepare 124 compounds with other rare earths such as  $\text{Nd}$  and  $\text{Sm}$ , which is otherwise not possible under ambient pressures.

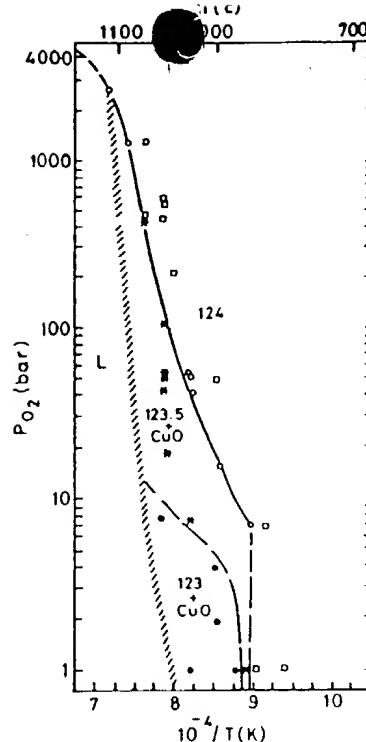


Figure 2. Phase diagram of the 124, 247 and 123 cuprates (from [43]).

A variety of substitutions has been carried out at the Y, Ba and Cu sites in  $\text{YBa}_2\text{Cu}_4\text{O}_8$  under high oxygen pressures. Yttrium can be substituted up to 10% by Ca in  $\text{YBa}_2\text{Cu}_4\text{O}_8$  giving a  $T_c$  of  $\sim 90$  K [46]; 20% Ba has been substituted by Sr without affecting the  $T_c$  [47]. Single-phase iron-substituted  $\text{YBa}_2\text{Cu}_{4-x}\text{Fe}_x\text{O}_8$  ( $0 \leq x \leq 0.05$ ) has been prepared at an oxygen pressure of 200 bar [48]; the  $T_c$  falls monotonically with increasing iron concentration.

Bordet *et al* [49] first reported the preparation of  $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$  under oxygen pressures of 100–200 bar. It was soon realized that  $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$  can be synthesized by the ceramic method under an oxygen pressure of 1 atm by a procedure similar to that employed for  $\text{YBa}_2\text{Cu}_4\text{O}_8$ , except for the difference in the sintering temperature [36]. There is a narrow stability region between 1123 K and 1143 K for the 247 cuprate to be synthesized under 1 atm oxygen pressure. The best sintering temperature at which the 247 cuprate is formed is 1133 K. Other rare-earth 247 cuprates,  $\text{Ln}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$  ( $\text{Ln} = \text{Dy, Er}$ ), can also be prepared by this method [36, 38]. About 5% of Y can be replaced by Ca in  $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$  and the  $T_c$  increases to 94 K [42]. Substitution of La at the Ba site is limited to  $\sim 10\%$  in  $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ , where the  $T_c$  decreases continuously with increasing lanthanum content [42].

Synthesis of 247 cuprates by the high-pressure oxygen method is generally carried out at 1203 K at an oxygen pressure of around 19 bar (for 8 h). This step is followed by slow cooling (typically  $5^\circ\text{C min}^{-1}$ ) to room temperature at the same pressure [50]. Other rare-earth 247 compounds,  $\text{Ln}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$  ( $\text{Ln} = \text{Eu, Gd, Dy, Ho}$

and Er), have been prepared in the oxygen pressure range of 14–35 bar [50]. Preparative conditions for the 124 and 247 cuprates are given in table 2.

#### 2.4. Bismuth cuprates

Although the ceramic method is widely employed for the synthesis of superconducting bismuth cuprates of the type  $\text{Bi}_2(\text{Ca}, \text{Sr})_{n+1}\text{Cu}_n\text{O}_{2n+4+\delta}$ , it is generally difficult to obtain monophasic compositions, due to various factors [51, 52]. Both thermodynamic and kinetic factors are clearly involved in determining the ease of formation as well as phasic purity of these cuprates. The  $n = 1$  member (2201) of the formula  $\text{Bi}_2\text{Sr}_2\text{CuO}_6$  appears to be stable around 1083 K and the  $n = 2$  member,  $\text{Bi}_2(\text{Ca}, \text{Sr})_3\text{Cu}_2\text{O}_8$  (2122) around 1113 K. The  $n = 3$  member,  $\text{Bi}_2(\text{Ca}, \text{Sr})_4\text{Cu}_3\text{O}_{10}$  (2223), can be obtained close to the melting point (1123 K) after heating for several days or even weeks. Of all the members of the  $\text{Bi}_2(\text{Ca}, \text{Sr})_{n+1}\text{Cu}_n\text{O}_{2n+4+\delta}$  family, the  $n = 2$  member (2122) seems to be most stable.  $\text{Bi}_2\text{O}_3$ , which is often used as one of the starting materials, melts at around 1103 K. Increasing the reaction temperature therefore leads to preferential loss of volatile  $\text{Bi}_2\text{O}_3$ . This results in micro-inhomogeneities and the presence of the unreacted oxides in the final product. Since these materials contain so many cations, partial reaction between various pairs of oxides leading to the formation of impurity phases in the final product cannot easily be avoided. A noteworthy structural feature of all these bismuth cuprates is the presence of superlattice modulation; the modulation has nothing to do with superconductivity.

Most of the above problems have been overcome by employing the matrix reaction method [53, 54]. This method reduces the number of reacting components and gives better products. In this method, synthesis is carried out by reacting the oxide matrix made from  $\text{CaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{CuO}$  with  $\text{Bi}_2\text{O}_3$  in the temperature range of 1083–1123 K in air for a minimum period of 48 h. Quenching the samples in air from the sintering temperature or heating in a nitrogen atmosphere improves the superconducting properties of bismuth cuprates. The matrix reaction method yields monophasic  $n = 2$  (2122) and  $n = 3$  (2223) compositions showing  $T_c$  values of 85 K and 110 K respectively [55, 56]. Partial melting for a short period (~5 min) also favours the rapid formation of the  $n = 2$  (2122) and the  $n = 3$  (2223) members.

The  $n = 1$  member,  $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ , showing  $T_c$  in the range 7–22 K is a rather complicated system and has two structurally different phases near the stoichiometric composition [51, 57–60]. Many workers have varied the Bi/Sr ratio and obtained single-phase materials with a  $T_c$  of 10 K at a composition which is strontium deficient,  $\text{Bi}_{2.1}\text{Sr}_{1.9}\text{CuO}_6$ , [60, 61]. This cuprate is best prepared by reacting the oxides and/or carbonates of the constituent metals at 1123 K in air for extended periods of time. In figure 3 we show the phase diagram of the Bi–Sr–Cu–O system. The phase diagram of the

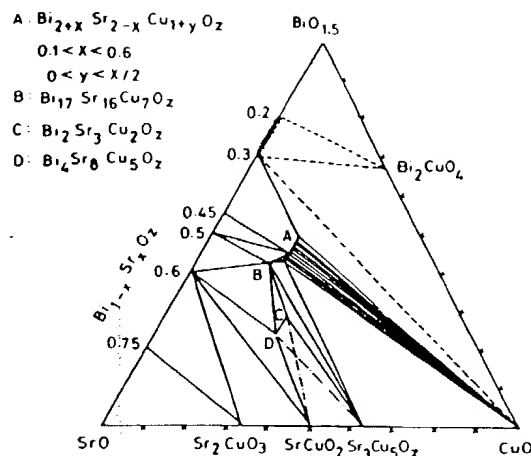


Figure 3. Phase diagram of the Bi–Sr–Cu–O system at 1110 K in air (from [60]).

$\text{Bi}_2\text{O}_3$ – $\text{SrO}$ – $\text{CaO}$ – $\text{CuO}$  system at a constant Cu content is shown in figure 4.

Substitution of a small amount of lead for bismuth results in good superconducting samples of  $n = 2$  (2122) and  $n = 3$  (2223) members. A number of workers have therefore preferred to synthesize both  $n = 2$  (2122) and  $n = 3$  (2223) members with substitution of lead up to 25% in place of bismuth [58, 63–66]. They are obtained either by direct reaction of oxides and/or carbonates of the cations or by the matrix reaction method.

Other than the matrix reaction method, melt quenching (glass route) [67, 68] and a semi-wet method [6] have been employed for the synthesis of superconducting bismuth cuprates. In the melt quenching method the mixture of starting materials (in the form of oxides and/or carbonates) is melted in a platinum or alumina crucible around 1473 K for a short period in air and then quenched in liquid nitrogen. The quenched specimens are given an annealing treatment around 1103 K in air to obtain the superconducting crystalline cuprates. This method has been shown to produce both  $n = 2$  (2122) and lead-doped  $n = 3$  (2223) members.

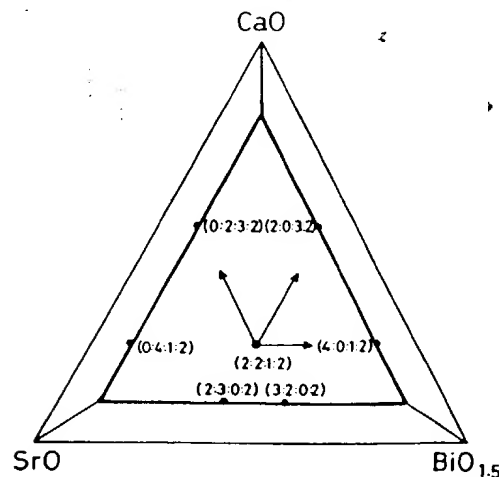


Figure 4. Section through the phase diagram of the  $\text{Bi}_2\text{O}_3$ – $\text{SrO}$ – $\text{CaO}$ – $\text{CuO}$  system at a constant CuO content of 28.6 mol% (from [62]).

of the bismuth cuprates, essentially in the form of 100%. The semi-wet method involves the solid-state reaction between two precursors which are coprecipitated separately. For example, in the preparation of  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ , a precipitate of Pb, Sr and Ca (as carbonates) and one of Bi and Cu (as oxalates) are reacted at 1138 K in air for a minimum period of 72 h. The duration of the reaction for the formation of 2223 phase is drastically reduced by this method.

The starting composition of the reactant materials plays an important role in the synthesis of these cuprates. For example, strontium deficiency in the  $n = 1$  (2201) member favours monophasic compositions [59, 61]. Strontium deficiency also helps in obtaining a phase-pure  $n = 2$  (2122) member [70]. Starting with a 4:3:3:4 stoichiometry of Bi:Ca:Sr:Cu, it has been possible to obtain a monophasic 2122 member [54, 71]. The  $n = 3$  (2223) phase, on the other hand, is either obtained through the substitution of Bi by Pb (up to 25%) or by taking an excess of Ca and/or Cu [63–66, 72]. The problem of balancing between phasic purity and high  $T_c$  of the cuprate gives rise to some difficulty in the synthesis of these cuprates. The coexistence of some of the members of the homologous series, especially in the form of polytypic intergrowths of different layered sequences, is also a problem. This problem is also encountered with thallium cuprates [73, 74].

The  $n = 4$  phase,  $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Ca}_3\text{Sr}_2\text{Cu}_4\text{O}_{12}$ , which was observed in an electron micrograph along with  $n = 3$  phase as an intergrowth, was synthesized in bulk by Rao *et al* [75] (with a small proportion of the  $n = 3$  phase) by the ceramic method. The  $n = 4$  phase has a slightly lower  $T_c$  (103 K), than the  $n = 3$  phase. This cuprate has also been prepared by Losch *et al* [75].

A variety of substitutions has been carried out in superconducting bismuth cuprates employing the ceramic method [58, 76–79]; some of them are noteworthy. For example, the simultaneous substitution of Bi by Pb and Sr by La in  $\text{Bi}_2\text{Sr}_2\text{CuO}_6$  results in a modulation-free superconductor of the formula  $\text{BiPbSr}_{1+x}\text{La}_{1-x}\text{CuO}_6$  with  $T_c$  increased to 24 K [77]. Similarly, co-substitution of Bi by Pb and Ca by Y in the  $n = 2$  member (2122) gives a modulation-free superconductor,  $\text{BiPbY}_{0.5}\text{Ca}_{0.5}\text{Sr}_2\text{Cu}_2\text{O}_8$  with a  $T_c$  of 85 K [77]. Rare-earth substitution for Ca in  $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$  causes the  $T_c$  to go up to 100 K without the introduction of the  $n = 3$  phase [58, 78]. As mentioned earlier, the  $n = 3$  phase is stabilized by the partial substitution of lead in place of bismuth [63–65]. Another significant discovery is the iodine intercalation of the Bi-2122 superconductor [80]. Intercalation does not greatly affect the superconducting properties of the material; clearly, superconductivity is confined to the two-dimensional  $\text{CuO}_2$  sheets in these materials.

Synthesis of a new series of superconducting cuprates of the general formula  $\text{Bi}_2\text{Sr}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_{10}$  (Bi-2222 phase with  $\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}$ ) containing a fluorite-like  $(\text{Ln}_{1-x}\text{Ce}_x)_2\text{O}_2$  layer between the two  $\text{CuO}_2$  sheets has been possible by the ceramic method [81]. Partial substitution of bismuth by lead increases

the  $T_c$  of this phase to 90 K [82]. High-pressure synthesis at 80 atm of  $\text{O}_2$  seems to stabilize the 2222 structure with other rare earths [83].

As mentioned earlier, one does not start with an exact stoichiometric composition to obtain the desired final product in the case of superconducting bismuth cuprates. Although structural studies (see for example [84]) indicate the presence of bismuth atoms over strontium and calcium sites as well, it is not possible to prescribe an exact initial composition to obtain the desired final stoichiometry. For example, starting from a nominal composition of  $(\text{Bi}_{0.7}\text{Pb}_{0.3})\text{SrCaCu}_2\text{O}_7$ , one ends up with the formation of the  $n = 3$  (2223) member [65]. Therefore, for the purpose of characterizing the various members of the superconducting bismuth cuprates, one starts with some arbitrary composition and varies the synthetic conditions suitably to obtain the desired final product in pure form. The actual compositions of the final cuprate are quite unexpected (e.g.  $\text{Bi}_{1.83}\text{Pb}_{0.30}\text{Sr}_{2.04}\text{Ca}_{1.68}\text{Cu}_3\text{O}_9$ ) as found from analytical electron microscopy [85]. In table 3 we have summarized the preparative conditions of all the members of  $\text{Bi}_2(\text{Ca}, \text{Sr})_{n+1}\text{Cu}_n\text{O}_{2n+4+\delta}$  family.

## 2.5. Thallium cuprates

The conventional ceramic method employed for the synthesis of 214, 123 and bismuth cuprates has to be modified in the case of thallium cuprates of the  $\text{Tl}_2\text{Ca}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+4}$ ,  $\text{TlCa}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+3}$  and  $\text{TlCa}_{n-1}\text{Sr}_2\text{Cu}_n\text{O}_{2n+3}$  families due to the toxicity and volatility of thallium oxide. In the early days, the reaction was carried out in an open furnace in air or oxygen atmosphere at high temperatures (1150–1180 K) for 5–10 min [86, 87]. In a typical procedure, the mixture of reactants in the form of a pellet was quickly introduced into the furnace maintained at the desired temperature. Since melt–solid reactions take place faster than solid–solid reactions, the product was formed quickly by this method [87]. Although this method requires a very short duration of heating, it results in the loss of thallium, leading to the danger of inhaling thallium oxide vapour. Some workers have taken certain precautions not to release the  $\text{Tl}_2\text{O}_3$  vapour into the open laboratory, but the method is still not recommended. Furthermore, the formation of the desired phase is not ensured under the open reaction conditions. Synthesis of thallium cuprates has therefore been carried out in closed containers (sealed tubes) by most workers. By this method, both polycrystalline samples and single crystals can be prepared, since the reaction is carried out over longer periods. Better control of stoichiometry, homogeneity of phases and the total avoidance of the inhalation of toxic thallium oxide vapours are some of the advantages of carrying out sealed tube reactions.

Closed reaction conditions have been achieved in different ways. The reactant mixture is sealed in gold [88] or silver tubes [89] or in a platinum [90] or nickel

Table 3. Preparative conditions for the synthesis of bismuth cuprates by the ceramic method.

Starting composition	Conditions <sup>a</sup>		Product	$T_c$ (K)	Ref.
	Temp. (K)	Time			
$\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_x$	1103	2 d	2201 major phase	20	[51]
$\text{Bi}_2\text{Sr}_2\text{CuO}_6$	1123	1 d	2201 major phase	9	[57]
$\text{Bi}_{2.1}\text{Sr}_{1.9}\text{CuO}_x$	1123	2 d	Single phase	10	[59, 61]
$\text{BiPbSr}_{1.4}\text{La}_{1.6}\text{CuO}_6$	1150	1 d	Single phase	24	[77]
$\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$	1103	5 d	Single phase	85	[61]
$\text{Bi}_2\text{Ca}_{1.5}\text{Sr}_{1.5}\text{Cu}_2\text{O}_8^b$	1103	3 d	2122 major phase	80	[53]
$\text{Bi}_4\text{Ca}_3\text{Sr}_3\text{Cu}_4\text{O}_x$	1108	2 d	2122 single phase	85	[71]
$\text{Bi}_2\text{Sr}_{1.7}\text{CaCu}_2\text{O}_x$	1113	3 d	2122 single phase	85	[70]
$\text{BiPbSr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_8$	1200	1 d	2122 single phase	85	[77]
$\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x^b$	1140	5 d	2223 major phase	120	[55]
$\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Ca}_{2.5}\text{Sr}_{1.5}\text{Cu}_3\text{O}_x^b$	1100	4 d	2223 major phase	105	[64]
$\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_x$	1153	10 d	2223 single phase	110	[72]
$\text{Bi}_{0.7}\text{Pb}_{0.3}\text{SrCaCu}_{1.8}\text{O}_x$	1153	5 d	2223 major phase	105	[65]
$\text{BiCaSrCu}_2\text{O}_x$	1143	5 d	2223 major phase	120	[65]
$\text{Bi}_{3.2}\text{Pb}_{0.8}\text{Ca}_5\text{Sr}_4\text{Cu}_7\text{O}_x$	1133	5 d	2223 major phase	108	[64]
$\text{Bi}_2\text{Gd}_{1.7}\text{Ce}_{0.3}\text{Sr}_3\text{Cu}_2\text{O}_{10}$	1273	10 h	2222 single phase	30	[81]

<sup>a</sup> All the preparations carried out in air.<sup>b</sup> Obtained by matrix reaction method.

alloy (Inconel) container [91] closed tightly with a silver lid. Alternatively, the reactant mixture is taken in the form of a pellet, wrapped in a platinum [92] or gold [93] foil and then sealed in a quartz tube. This method has the advantage of carrying out the reaction under a vacuum. Some workers place the reactant pellet in an alumina crucible [94] which is then sealed in a quartz ampoule. Thallium-excess starting compositions have been employed by a few workers to compensate for the thallium loss during the reaction [95].

In the preparation of the thallium cuprates, the matrix reaction method is often employed. Here, a mixed oxide containing all the metal ions other than the volatile thallium oxide is first prepared by reacting the corresponding oxides and/or carbonates around 1200 K for 24 h in air [89, 96]. The freshly prepared mixed oxide is then taken with a calculated quantity of  $\text{Tl}_2\text{O}_3$  and heated at appropriate temperatures in a sealed tube. This method is desirable when a carbonate is used as the starting material. Some of the thallium cuprates have been prepared by a modified matrix method [97] wherein a thallium-containing precursor such as  $\text{Ba}_2\text{Tl}_2\text{O}_5$  is prepared first and then reacted with other components under closed conditions. Thallium-containing precursors are less volatile than  $\text{Tl}_2\text{O}_3$  so that the loss of thallium is minimized during the preparation.

Thermodynamic and kinetic factors associated with the synthesis of thallium cuprates are complex due to the existence of various phases which are structurally related and which can therefore intergrow with one another. In fact, one of the common defects that occurs in the thallium cuprates is the presence of random intergrowths between the various layered phases [98]. Furthermore, many of the thallium, lead and bismuth superconductors are metastable phases which are entropy stabilized [99]. The temperature of the reac-

tion, the sintering time and the starting composition are therefore all crucial to obtaining monophasic products (table 4).

The effect of the starting composition is best illustrated by the formation of the  $n = 3$  phase of the bilayer thallium cuprates ( $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$ ). Synthesis of this compound starting from the stoichiometric mixture of the oxides corresponding to the ideal composition often yields the  $n = 2$  member of the family. It was found that starting with compositions rich in Ca and/or Cu (namely  $\text{TlCa}_3\text{BaCu}_3\text{O}_x$ ,  $\text{Tl}_2\text{Ca}_4\text{Ba}_2\text{Cu}_5\text{O}_x$ ) yielded a nearly pure  $n = 3$  phase [90, 98, 100]. The actual composition is, however, close to  $\text{Tl}_{1.7}\text{Ba}_2\text{Ca}_{2.3}\text{Cu}_3\text{O}_x$ . In the case of  $\text{TlCaBa}_2\text{Cu}_2\text{O}_7$  (1122) starting from a stoichiometric mixture of oxides corresponding to the ideal stoichiometry always yielded a mixture of 1122 and 2122 phases, the relative proportion of the two being dependent on the conditions. It has been demonstrated recently [101] that thallium-deficient compositions corresponding to  $\text{Tl}_{1-\delta}\text{CaBa}_2\text{Cu}_2\text{O}_x$  ( $\delta = 0.0$  to  $0.3$ ) yield better monophasic 1122 materials.

The thallium content of the material not only determines the number of  $\text{Tl-O}$  layers but controls the hole concentration. As mentioned earlier, one of the good starting compositions to obtain  $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$  (2223) is  $\text{TlCa}_3\text{BaCu}_3\text{O}_x$  (1313) which bears little relation to the composition of the final product. Another example is the formation of the  $n = 4$  phase,  $\text{TlCa}_3\text{Ba}_2\text{Cu}_4\text{O}_x$  (1324). Detailed studies [102] have shown that the 2223 phase formed initially transforms to the 1223 phase with an increase in the duration of heating. After prolonged sintering, the 1324 phase is formed at the expense of the 1223 phase. Similar transformations have also been observed in the formation process of  $\text{TlCa}_4\text{Ba}_2\text{Cu}_5\text{O}_x$  with five Cu-O layers [103].

The Sr analogue of  $\text{TlCa}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+3}$  cannot be prepared in pure form. However, they are stabilized by

Starting composition	Conditions			Product	$T_c$ (K)	Ref.
	Temp. (K)	Time	Gas			
$Tl_2Ba_2CuO_8$	1148	3 h	Sealed gold tubes	2201 single phase	84	[88]
$Tl_2CaBa_2Cu_2O_8$	1173	6 h	Sealed gold tubes	2122 single phase	98	[88]
	1150	3 h	Sealed silica ampoule	2122 single phase	95	[98]
$Tl_2Ca_4Ba_2Cu_5O_8$	1150	0.5 h	Sealed silica ampoule	2122 single phase	95	[98]
$Tl_4Ca_3Ba_4Cu_5O_8$	1150	0.5 h	Sealed silica ampoule	2122 single phase	95	[98]
$Tl_2Ca_2Ba_2Cu_3O_{10}$	1173	6 h	Sealed gold tubes	2223 major phase	105	[88]
	1123	20 min	Sealed silica ampoule	2223 major phase	106	[95]
	1103	12 h				
$TlCa_3BaCu_3O_8$	1153	3 h	Sealed silica ampoules	2223 major phase	125	[100]
$Tl_2CaBa_2Cu_3O_8$	1153	3 h	Sealed silica ampoules	2223 major phase	108	[100]
$TlBa_{1.2}La_{0.8}CuO_5$	1163	3 h	Sealed silica ampoules	1021 single phase	40	[111]
$TlSrLaCuO_5$	1170	2 h	Sealed silica ampoules	1021 single phase	40	[109]
$TlSr_{2.6}Nd_{0.4}Cu_2O_7$	1170	2 h	Sealed silica ampoules	1122 major phase	80	[110]
$TlCaBa_2Cu_2O_7$	1170	3 h	Sealed silica ampoules	1122 major phase + 2122 impurity	90	[101]
$Tl_{0.8}CaBa_2Cu_2O_7$	1170	3 h	Sealed silver tubes	1122 major phase	90	[101]
$(Tl_{0.5}Pb_{0.5})CaSr_2Cu_2O_7$	1170	3 h	Sealed silica ampoules	1122 single phase	90	[104]
$Tl(Ca_{0.5}Y_{0.5})Sr_2Cu_2O_7$	1170	3 h	Sealed silver tubes	1122 single phase	90	[92]
$TlCa_2Ba_2Cu_3O_9$	1163	6 h	Sealed silica ampoules	1223 single phase	115	[94]
$(Tl_{0.5}Pb_{0.5})Ca_2Sr_2Cu_3O_9$	1198	3–12 h	Sealed gold tubes	1223 single phase	122	[105]
$Tl_{0.5}Pb_{0.5}Sr_4Cu_3O_8$	1170	2 h	Sealed silica ampoules	1223 major phase	60	[110]

partly substituting Tl by Pb (or Bi) or Ca by yttrium or a trivalent rare earth [92, 104–107]. Thus,  $Tl_{0.5}Pb_{0.5}Ca_{n-1}Sr_2Cu_nO_{2n+3}$  shows a  $T_c$  of  $\sim 90$  K for  $n = 2$  and  $\sim 120$  K for  $n = 3$ .  $TlCa_{0.5}Y_{0.5}Sr_2Cu_2O_7$  also shows a  $T_c$  of 90 K. These cuprates in the Tl/Pb–Ca/Ln–Sr–Cu–O systems are prepared in a manner similar to the Tl–Ca–Ba–Cu–O system except that  $SrCO_3$  is used in place of  $BaCO_3$  or  $BaO_2$ .  $Sr_4Tl_2O_7$  has also been used as a starting material in some instances [97]. The  $n = 1$  member,  $TlM_2CuO_5$  ( $M = Sr$  or  $Ba$ ) is also stabilized by the substitution of Pb or Bi for Tl or a trivalent rare earth for Sr or Ba [108–111]. All these compounds showing a  $T_c$  of 40 K have been prepared by the matrix reaction method.

Single thallium layer cuprates of the general formula  $Tl_{1-x}A_{2-x}Ln_2Cu_2O_9$  with  $A = Sr, Ba$ ;  $Ln = Pr$  (Nd, Ce) as well as  $Tl_{0.5}Pb_{0.5}(Ln_{1-x}Ce_x)_2Sr_2Cu_2O_9$  ( $Ln = Pr, Gd$ ) with a fluorite-type  $Ln_2O_3$  layer have been prepared by the ceramic method [112, 113]. The as-prepared materials are semiconductors. It has been shown by Liu *et al* [114] that annealing  $TlBa_2(Eu, Ce)_2Cu_2O_9$  (1222 phase) under an oxygen pressure of 100 bar induces superconductivity with a  $T_c$  of  $\sim 40$  K.

As in the case of bismuth cuprates, the final composition of thallium cuprates is unlikely to reflect the composition of the starting mixture. Structural studies [99, 115] have shown that there is cation disorder between Tl and Ca/Sr sites. Therefore, in order to obtain a superconducting composition corresponding to a particular copper content, one has to start with various arbitrary compositions and vary the synthesis conditions. The actual composition of the final product can be quite unexpected (e.g.  $Tl_{1.83}Ba_2Ca_{1.44}Cu_3O_9$  or  $Tl_{1.86}Ba_{2.01}CuO_9$ ) as shown by analytical electron microscopy [85]. In table 4 we have listed the pre-

parative conditions employed for the synthesis of thallium cuprates by the ceramic method.

## 2.6. Lead cuprates

The conditions for the synthesis of superconducting lead cuprates are more stringent than for the other copper oxide superconductors. Direct synthesis of members of the  $Pb_2Sr_2(Ln, Ca)Cu_3O_{8+\delta}$  ( $Ln = Y$  or rare earth) family by the reaction of the component metal oxides or carbonates in air or oxygen at temperatures below 1173 K is not possible because of the high stability of  $SrPbO_3$ -related perovskite oxides. Preferential loss of the more volatile  $PbO$  leads to micro-inhomogeneities. Furthermore, Pb in these compounds is in the 2+ state while part of the Cu is in the 1+ state. Synthesis has therefore to be carried out under mildly reducing conditions, typically in an atmosphere of  $N_2$  containing 1%  $O_2$ . The most common method that has been employed for the synthesis of these lead cuprates is the matrix reaction method [116]. For  $Pb_2Sr_2(Ln, Ca)Cu_3O_{8+\delta}$  ( $Ln = Y$  or rare earth), a mixed oxide containing all the metal ions except Pb is made by reacting  $SrCO_3$ ,  $Ln_2O_3$  or  $Y_2O_3$ ,  $CaCO_3$  and  $CuO$  in the appropriate ratios around 1223 K in air for 16 h. The mixed oxide is then taken with an appropriate amount of  $PbO$ , ground thoroughly, pelletized and heated in the 1133–1198 K range in a flowing stream of nitrogen containing 1%  $O_2$  for periods between 1 and 16 h. Generally, short reaction times and quenching the product from the sintering temperatures into liquid nitrogen in the same atmosphere gives better-quality samples. Even though this is the common method for preparing  $Pb_2Sr_2(Ln, Ca)Cu_3O_{8+\delta}$ , it is not always easy to obtain samples exhibiting good, reproducible

superconducting properties. The lead cuprates from the method described above generally show broad transitions in the  $R-T$  curves with negative temperature coefficients of resistance above  $T_c$ .

Studies of the dependence of  $T_c$  on the calcium concentration in the  $\text{Pb}_2\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_{8+\delta}$  system [117] have shown that heating the samples near the melting point between 1198 and 1228 K for 2 h and post-annealing in flowing nitrogen gas at a temperature between 673 and 773 K improves the superconducting properties of the samples dramatically. Direct one-step synthesis has been achieved [118] by reacting the metal oxides in sealed gold tubes around 1223 K. An alternative route to the direct synthesis from metal oxides and/or carbonates has also been demonstrated [119]. Superconductivity near 70 K has been reported in Ca-free  $\text{Pb}_2\text{Sr}_2\text{LnCu}_3\text{O}_{8+\delta}$  ( $\text{Ln} = \text{Y}$  or rare earth) employing the vacuum annealing procedure [120]. Substitution of Pb by Bi in  $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_{8+\delta}$  has also been carried out by the ceramic method [121]. About 30% of Pb can be substituted by Bi, and such a substitution increases the  $T_c$  up to 100 K. The  $n = 0$  member of the  $\text{Pb}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Ln}_x)_n\text{Cu}_{2+n}\text{O}_{6+2n+\delta}$  series (namely  $\text{Pb}_2(\text{SrLa})\text{Cu}_2\text{O}_{6+\delta}$ ) has been prepared successfully by this matrix reaction method [122].

Unlike the 2213-type lead cuprates, superconducting 1212-type lead cuprates of the formula  $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$  are synthesized in an oxidizing atmosphere. Several authors have reported direct synthesis as well as reactions under closed conditions [123–127]. In the direct synthesis of these cuprates, care is taken to prevent the loss of Pb by wrapping pellets in gold or platinum foil [127]. Rouillon *et al* [125, 126] have reported the synthesis of 1212 lead cuprates by the direct reaction of the component oxides in evacuated silica ampoules. This method has

the advantage of adjusting the oxygen partial pressure required for the synthesis. Both 2213-type and 1212-type lead cuprates have been prepared using the nitrates of the metal ions as the starting materials [128]. Although this procedure yields 2213 or 1212 phases in a single step, the product obtained always has impurities such as  $\text{Y}_2\text{O}_3$ ,  $\text{CuO}$  etc.

A superconducting lead cuprate of the formula  $(\text{Pb}, \text{Cu})(\text{Eu}, \text{Ce})_2(\text{Sr}, \text{Eu})_2\text{Cu}_2\text{O}_9$  (1222 phase) containing a fluorite layer has been prepared by the direct reaction of the component metal oxides at 1273 K in oxygen atmosphere [129].

High-pressure ceramic synthesis has been employed to prepare lead cuprates of the 1212 type [130, 131]. In order to prepare  $\text{Pb}_{0.5}\text{Cu}_{0.5}\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{7-\delta}$ , sintering is carried out at 1213 K for 15 h under an oxygen pressure of 100 bar followed by fast cooling to 373 K. The samples obtained from high-pressure oxygen treatment show higher  $T_c$ s than those processed at 1 bar pressure of oxygen. Substitution of Y by other rare earths has been possible by this high-oxygen-pressure method [131]. All the rare-earth substituted compounds are superconducting with  $T_c$ s in the 50–70 K range. The  $T_c$  decreases with increase in the size of the rare earth. In table 5 we summarize the conditions for the synthesis of the various lead cuprates by the ceramic method.

## 2.7 Electron-doped superconductors

All the cuprates discussed till now are hole superconductors. Synthesis of electron-doped cuprate superconductors of the type  $\text{Ln}_{2-x}\text{M}_x\text{CuO}_{4-\delta}$  ( $\text{Ln} = \text{Nd}, \text{Pr}, \text{Sm}, \text{Eu}$ ;  $\text{M} = \text{Ce}, \text{Th}$ ), possessing the  $T'$  structure, is generally achieved by the ceramic method [132–134]. The conditions of synthesis are more stringent since the

**Table 5.** Conditions for the synthesis of lead cuprates by the ceramic method.

Compound	Starting materials	Conditions			Comments	$T_c$ (K)	Ref.
		Temp. (K)	Time	Gas			
$\text{Pb}_2\text{Sr}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_3\text{O}_{8+\delta}$	$\text{PbO} + \text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_x$ matrix	1143	1–16 h	$\text{N}_2 + 1\% \text{O}_2$		78	[116]
	$\text{PbO}, \text{PbO}_2, \text{CaO}_2, \text{SrO}_2, \text{Y}_2\text{O}_3, \text{CuO}$	1223	12–48 h		Sealed gold tubes	78	[118]
	$\text{PbO}, \text{SrCO}_3, \text{Y}_2\text{O}_3, \text{CaCO}_3, \text{CuO}$	1073	15 h	air			
		1173	2 h	air			
		1073	1–5 h	$\text{N}_2$		78	[119]
$\text{Pb}_2\text{Sr}_{0.8}\text{La}_{1.2}\text{Cu}_2\text{O}_{6+\delta}$	$\text{PbO}, \text{La}_2\text{O}_3, \text{Sr}_2\text{CuO}_3, \text{CuO}$	1083	6 h	$\text{N}_2$	2202 major phase + $\text{Pb}_2\text{LaCu}_{0.3}\text{O}_x$ impurity	26	[122]
$(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{SrLaCuO}_x$	$\text{PbO}, \text{SrCO}_3, \text{La}_2\text{O}_3, \text{CuO}$	1073	5 h	air		25	[123]
$(\text{Pb}_{0.7}\text{Cu}_{0.3})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$		1273	2 h	$\text{O}_2$			
	$\text{PbO}, \text{SrCO}_3, \text{Y}_2\text{O}_3, \text{CaCO}_3, \text{CuO}$	1123	10 h	air		50	[124]
		1273	1 h	$\text{O}_2$	1212 major phase + $\text{Sr}_5\text{Pb}_3\text{CuO}_{12}$ impurity	47	[127]
$(\text{Pb}_{0.5}\text{Sr}_{0.5})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_x$	$\text{PbO} + \text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_{2.3}\text{O}_x$ matrix	1243	3 h	$\text{O}_2$	1212 major phase + $\text{Sr}_5\text{Pb}_3\text{CuO}_{12}$ impurity	100	[125]
	$\text{PbO}, \text{PbO}_2, \text{Sr}_2\text{CuO}_3, \text{Y}_2\text{O}_3, \text{CaO}_2, \text{Cu}_2\text{O}, \text{CuO}$	1108–1223	1–10 h		Evacuated silica tubes	80	[126]
	$\text{PbO}_2, \text{PbO}, \text{SrO}_2, \text{SrCuO}_2, \text{Y}_2\text{O}_3, \text{CaO}, \text{CuO}$	1108–1223	1–10 h				
$(\text{Pb}_{0.8}\text{Cu}_{0.2})\text{Sr}_{1.75}\text{Eu}_{0.25}\text{Cu}_2\text{O}_x$	$\text{PbO}, \text{SrCO}_3, \text{Eu}_2\text{O}_3, \text{CeO}_2, \text{CuO}$	1123	10 h	air	Single phase 1222	25	[129]
		1323	1 h	$\text{O}_2$			



valence of copper has to be less than 2+ in the material, by making sure that the extra electron donated by  $\text{Ce}^{4+}$  or  $\text{Th}^{4+}$  does not increase the oxygen content of the cuprate. For this reason, samples after calcination and sintering at 1323 K in air (for 24 h) are annealed in a reducing atmosphere (typically Ar,  $\text{N}_2$  or dilute  $\text{H}_2$ ) at 1173 K to achieve superconductivity. Samples prepared in this manner show a negative temperature coefficient of resistance above  $T_c$  in the  $R$ - $T$  curves; the resistivity drop at  $T_c$  is also not sharp. An alternative synthetic route involves the reaction of pre-reacted  $\text{NdCeO}_{3.5}$  material with the required amounts of  $\text{Nd}_2\text{O}_3$  and  $\text{CuO}$  at 1253 K for a minimum period of 48 h in flowing oxygen [135]. The samples are then rapidly quenched from 1253 K in an argon atmosphere to achieve superconductivity. This procedure eliminates the slow diffusion of Ce throughout the  $\text{Nd}_2\text{CuO}_{4-x}$  host and gives uniform concentrations of cerium and oxygen. Samples obtained from this route show a sharp transition at 21 K.

Superconductivity with a  $T_c$  of 25 K is induced by doping fluorine for oxygen in  $\text{Nd}_2\text{CuO}_4$ . This has been accomplished by taking  $\text{NdF}_3$  as one of the initial reactants [136]. Substitution of either Ga or In for copper in non-superconducting  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-x}$  also induces superconductivity [137, 138].

## 2.8. Infinite-layer cuprates

Discovery of superconductivity in cuprates containing infinite  $\text{CuO}_2$  layers has been of great importance in understanding the phenomenon. Very high pressures have been employed for obtaining the infinite-layer cuprates. Both hole-doped (e.g.  $\text{Ca}_{1-x}\text{Sr}_x\text{CuO}_2$ ) and electron-doped ( $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ ) infinite-layer cuprate superconductors with a maximum  $T_c$  of 110 K have been reported [139–142]. Infinite-layered cuprates of the type  $(\text{Ba}, \text{Sr})\text{CuO}_2$ ,  $(\text{Ca}, \text{Sr})\text{CuO}_2$  are synthesized in an oxidizing atmosphere under high hydrostatic pressure [139, 140, 142]. Electron-doped  $\text{Sr}_{0.86}\text{Nd}_{0.14}\text{CuO}_2$  is also prepared under high hydrostatic pressures [141]. Metal nitrates are generally used as the starting materials since carbonates of Ba, Sr and Ca have high decomposition temperatures. After decomposing the metal nitrates at around 873–1123 K in air, the product is subjected to high pressure to obtain the superconducting phases.  $\text{Sr}_{0.86}\text{Nd}_{0.14}\text{CuO}_2$ , which superconducts at 40 K, is made under a hydrostatic pressure of 25 kbar at 1273 K. Superconducting  $(\text{Ca}, \text{Sr})\text{CuO}_2$  is prepared at 1273 K under 6 GPa pressure. Deficiency of Sr and Ca as well as the oxidizing atmosphere make this phase superconducting, and the oxidizing atmosphere is provided by heating a capsule containing  $\text{KClO}_4$  along with the sample. This cuprate has a  $T_c$  (onset) of 110 K.

## 3. Coprecipitation and precursor methods

Coprecipitation involves the separation of a solid containing various ionic species chemically bound to one

another from a liquid to a solution phase. A homogeneous coprecipitation process can result in the formation of crystalline or amorphous solids. Coprecipitation of well defined stoichiometry with respect to the metal ions is obtained only when the following conditions are satisfied.

- (i) The precipitating agent is a multivalent organic compound which can coordinate with more than one metal ion, and the precipitation rate is fast.
- (ii) The solid precipitating out of the solution should be really insoluble in the mother liquor.

The anions generally preferred for coprecipitation of oxidic materials are carbonates, oxalates, citrates etc. The same is true of high- $T_c$  cuprates. The precipitates in some instances could be genuine precursors or solid solutions [5, 6]. It is well known that precursor solid solutions drastically bring down diffusion distances for the cations and facilitate reactions in the solid state. We shall not distinguish precursor solid solutions precipitated from solutions from other precursors in this discussion.

The precipitates (carbonate, oxalate etc) are heated at appropriate temperatures in a suitable atmosphere to obtain the desired cuprate. Some of the advantages of the coprecipitation technique over the ceramic method are an homogeneous distribution of components, a decrease in the reaction temperatures and of the duration of annealing, a higher density and a lower particle size of the final product. The major drawback of this route is the control over the stoichiometry of the final product.

### 3.1. $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

La, Sr and Cu in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  are readily coprecipitated as carbonates [11, 12, 143]. For this purpose the required quantities of the various metal nitrates are dissolved together in distilled water. Alternatively, the corresponding oxides are dissolved in nitric acid to give a nitrate solution and the pH of the solution is adjusted to 7–8 by the addition of KOH solution. A solution of  $\text{K}_2\text{CO}_3$  of appropriate strength is then slowly added under stirring to give a light blue precipitate which is thoroughly washed. The precipitate is dried at 420 K and calcined at 1070 K for 8 h in air. The resulting black powder is ground and pelletized and sintered at 1270 K for 16 h in air to obtain monophasic  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ , superconducting at 35 K.

Instead of as carbonate, the metal ions are also readily precipitated as oxalate by the addition of either oxalic acid or potassium oxalate to the solution of metal nitrates [11, 12, 144, 145]. The precipitated oxalate is then decomposed to obtain the cuprate. This method has certain disadvantages:

- (i)  $\text{La}^{3+}$  in the presence of an alkali metal oxalate first yields lanthanum oxalate which further reacts with the precipitating agent to give a double salt. Control of stoichiometry therefore becomes difficult, leading to multiphasic products.

(ii) The relative solubilities of some of the oxalates also pose difficulties. For example,  $\text{SrC}_2\text{O}_4$  is nearly four times more soluble than  $\text{SrCO}_3$ .

### 3.2. $\text{YBa}_2\text{Cu}_3\text{O}_7$

$\text{YBa}_2\text{Cu}_3\text{O}_7$  and related 123 compounds can be obtained via coprecipitation of the component metals (from a nitrate solution) as a formate [146, 147], acetate [148], oxalate [12, 149–156], hyponitrite [157] or hydroxycarbonate [158, 159]. Some of these precipitates could be genuine precursor compounds as is indeed the case with the hyponitrite.

In oxalate coprecipitation [12, 149–152], oxalic acid solution of appropriate concentration is added to an aqueous solution of mixture of nitrates of Y, Ba and Cu and the pH of the solution is adjusted to 7.5 (by dilute  $\text{NH}_3$ ). The pale green slurry thus formed is digested for 1 h, filtered and dried. The oxalate is converted to orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  by heating at 1053 K in air for 5 days followed by oxygenation at 723 K. This procedure, even though successful in making superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  in small particulate form, often results in undesirable stoichiometry because of the moderate solubility of barium oxalate. Furthermore, rare-earth ions in the presence of ammonium oxalate give a double salt with the excess oxalate which competes with the precipitation of copper and barium oxalates. These difficulties can be overcome either by taking a known excess (wt%) of barium and copper or by using triethylammonium oxalate as the precipitant in aqueous ethanol medium [153–155]. The alcoholic medium decreases the solubility of barium oxalate and the pH of the solution is controlled *in situ*.

A better method of homogeneous coprecipitation of oxalates is that of Liu *et al* [156] using urea and oxalic acid. Urea, on heating, is hydrolysed liberating  $\text{CO}_2$  and  $\text{NH}_3$ , and thus gradually adjusting the pH throughout the solution. The  $\text{CO}_2$  liberated controls the bumping of the solution during digestion. The oxalate coprecipitation route is widely described in the literature. The reactive powders obtained by the oxalate coprecipitation method decrease the sintering temperature. The formation of  $\text{BaCO}_3$  in the intermediate calcinating step makes it difficult to obtain  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  in pure form.

Complete avoidance of the formation of  $\text{BaCO}_3$  during the synthesis is possible using the hyponitrite precursor [157]. The hyponitrite precursor is obtained from a nitrate solution of Y, Ba and Cu ions by the addition of an aqueous  $\text{Na}_2\text{N}_2\text{O}_2$  solution. The precipitate is converted into superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  by heating at around 973 K in an argon atmosphere, followed by oxygen annealing at 673 K. Although this route provides a convenient means of obtaining the 123 cuprate at much lower temperatures than with other methods, there is a possibility of contamination of alkali metal ions during the course of the precipitation.

$\text{YBa}_2\text{Cu}_3\text{O}_7$  can also be prepared by the hydroxycarbonate method [158, 159]. Here,  $\text{KOH}$  and  $\text{K}_2\text{CO}_3$

are employed to precipitate copper as the hydroxide and Y and Ba as the carbonates in the pH range of 7–8. By employing  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$ , complete precipitation as hydroxycarbonate is attained at a pH of  $\sim 13$ . The product from the above two procedures is homogeneous, showing sharp onset of superconductivity at 92 K. The possibility of contamination by alkali metal ions cannot, however, be avoided.

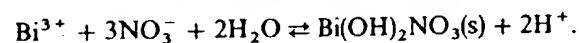
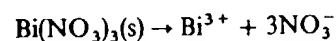
### 3.3. $\text{YBa}_2\text{Cu}_4\text{O}_8$

$\text{YBa}_2\text{Cu}_4\text{O}_8$  can be prepared by the oxalate route [160] wherein the solution of Y, Ba and Cu nitrates in water is added dropwise into oxalic acid–triethylamine solution under stirring. Complete precipitation of Y, Ba and Cu with the desired stoichiometry of 1:2:4 is achieved in the pH range of 9.3–11.3. The precipitated oxalates are filtered and dried in air at 393 K. The solid obtained is then heated in the form of pellets at 1078 K in flowing oxygen for 2–4 days. The product after quenching in air shows the 124 phase as the major product with a  $T_c$  of 79 K.

An alternative coprecipitation route for the synthesis of  $\text{YBa}_2\text{Cu}_4\text{O}_8$  is the method of Chen *et al* [161] in which the aqueous nitrate solution of the constituent metal ions is mixed with 8-hydroxyquinoline–triethylamine solution. The precipitated oxine is filtered, washed, dried and sintered at 1088 K in oxygen for 3 days to yield phase-pure  $\text{YBa}_2\text{Cu}_4\text{O}_8$  showing a  $T_c$  of 80 K. Ethylenediaminetetraacetic acid [161] as well as carbonate routes [162] have also been employed for the preparation of  $\text{YBa}_2\text{Cu}_4\text{O}_8$ . Coprecipitation using triethylammonium oxalate has been exploited for substituting Sr in place of Ba in  $\text{YBa}_2\text{Cu}_4\text{O}_8$  [163].

### 3.4. Bismuth cuprates

Very few coprecipitation studies have been carried out on the preparation of bismuth cuprates. One reason may be that despite the good sample homogeneity generally obtained through solution methods, the chemistry of bismuth cuprates is rather complex. It is not that easy to find compounds of all the constituent metal ions soluble in a common solvent; controlling the stoichiometry in these cuprates is also difficult in the coprecipitation procedure. Furthermore, bismuth nitrate, which is often used as one of the starting materials, decomposes in cold water to a basic nitrate precipitate as given by



This problem can be overcome to some extent by preparing the nitrate solution of bismuth in nitric acid or by starting with bismuth acetate instead of the nitrate.

Bidentate ligands such as the oxalate are found to react more rapidly than multidentate ligands such as citric acid [164–174] in the coprecipitation process. Complexes of oxalic acid are also more stable than



those obtained from a mononitrate in acetic acid, but there are some difficulties in controlling the stoichiometry because of the relative solubility of  $\text{BiC}_2\text{O}_4$  or  $\text{SrC}_2\text{O}_4$ .

A straightforward oxalate coprecipitation is achieved by dissolving the acetates of Bi, Ca, Sr and Cu in glacial acetic acid and then adding excess oxalic acid to the solution [164]. The oxalate precipitate is dried and decomposed at around 1073 K in air and processed in the 1103–1123 K range for periods ranging from 24 h to 4 days, depending on the starting composition. The  $n = 2$  (2122) member obtained by this procedure shows zero resistance at 83 K. In another procedure reported by Zhang *et al* [165], first the Sr/Ca/Cu nitrate solutions are mixed in the required molar ratio. Into this solution is poured a solution of bismuth nitrate prepared in nitric acid along with oxalic acid. The complete precipitation occurs at a pH of around 5 (attained by the addition of aqueous NaOH). This process involves the possibility of contamination of sodium ions; this has been circumvented by using  $\text{N}(\text{CH}_3)_4\text{OH}$  to adjust the pH of the solution [166] and complete precipitation of the oxalates occurs at a pH of 12. All these procedures, however, produce mixed-phase samples.

For the preparation of the monophasic lead-doped  $n = 3$  member (2223), oxalate coprecipitation has been found effective [167–174]. In the procedure reported by Chiang *et al* [171], the molar ratio of the chelating agent (oxalic acid) and the nitrate anions (from the metal nitrate solutions) is fixed at 0.5 and the pH, adjusted by  $\text{NH}_4\text{OH}$  solution, at which complete precipitation occurs is 6.7. The product from this method,  $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_7$ , after sintering at 1133 K in air for 72 h, shows a  $T_c$  of 110 K.

Coprecipitation as oxalates to prepare the lead-doped  $n = 3$  member (2223) has been achieved from an ethylene glycol medium using triethylammonium oxalate and oxalic acid [172]. A more easily controlled and reproducible oxalate coprecipitation procedure appears to be that of Shei *et al* [173] where in a mixture of triethylamine and oxalic acid is employed. The advantage of using triethylamine is that it has a higher basicity and a lower complexing ability towards Cu(II) than has ammonia. Control of the stoichiometry of the final product is therefore better obtained with this procedure; precipitation occurs in the pH range 1.5–2.2. The coprecipitated oxalates sintered at 1133 K in air for a minimum period of 72 h give monophasic  $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  with a  $T_c$  of 110 K. It is possible to avoid adjusting the pH in the coprecipitation of oxalates [174]. The procedure involves coprecipitating the oxalates from dilute acetate solutions instead of from nitrate solutions. The oxalates are then converted to nearly phase-pure  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  ( $T_c$  of 106 K) by sintering at 1123 K in air for 160 h.

Carbonate coprecipitation has also been carried out for the synthesis of superconducting bismuth cuprates [175, 176], but the method does not yield monophasic products.

Coprecipitation of thallium-based cuprates from aqueous solutions as oxalates is hindered by the solubility of thallium oxalate. However, Bernhard and Gritzner [177] have found that complete coprecipitation as oxalates can be achieved by starting with thallium acetate in glacial acetic acid medium. In the procedure reported for the preparation of the  $n = 3$  member (2223), stoichiometric amounts of thallium acetate,  $\text{CaCO}_3$ ,  $\text{BaCO}_3$  and copper acetate are dissolved in water containing glacial acetic acid. The solution containing all the cations is then added to a solution of oxalic acid (excess) under stirring. The precipitate, after digestion for 1 h, is filtered, washed and dried. The oxalates are heated in the form of pellets (wrapped in gold foil) at around 1173 K for 6 min in an oxygen atmosphere. The product after annealing in the same atmosphere shows 2223 as the major phase with a  $T_c$  of 118 K.

### 3.6. Lead cuprates

Carbonate coprecipitation is found to be satisfactory for the synthesis of representative members of superconducting lead cuprates [128] of 2213 and 1212 types, namely  $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_{8+\delta}$  and  $\text{Pb}_{0.5}\text{Sr}_{0.5}\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{7-\delta}$ . Coprecipitation as carbonates has been achieved by adding the nitrate solution of the constituent metal ions to an aqueous solution of sodium carbonate (in excess) under constant stirring. The carbonate precipitate thus obtained is washed and dried. The decomposed powder is heated in the form of pellets around 1153 K in a suitable atmosphere.  $\text{Pb}_2\text{Sr}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_3\text{O}_{8+\delta}$  obtained by this method after heating for 4 h in nitrogen containing 1%  $\text{O}_2$  showed 2213 as the major phase ( $T_c \sim 74$  K) with impurities such as  $\text{Y}_2\text{O}_3$ ,  $\text{CuO}$ . The 1212 phase obtained after heating in oxygen at 1153 K for 12 h showed a broad transition with a  $T_c$  (onset) of 100 K. This method has the advantage of single heating rather than the multistep procedures required in the other methods.

### 4. Sol-gel process

The sol-gel process is employed in order to get homogeneous mixing of cations on an atomic scale so that the solid state reaction occurs to completion in a short time and at the lowest possible temperature. The term sol often refers to a suspension or dispersion of discrete colloidal particles, while a gel represents a colloidal or polymeric solid containing a fluid component which has the internal network structure wherein both the solid and the fluid components are highly dispersed. In the sol-gel process a concentrated sol of the reactant oxides or hydroxides is converted to a semi-rigid gel by removing the solvent. The dry gel is heated at an appropriate

temperature to obtain the product. Most of the reactions in the sol-gel process occur via hydrolysis and polycondensation.

Two different routes for the sol-gel process are usually described in the literature for the synthesis of high- $T_c$  cuprate superconductors:

- (i) Via molecular precursors (e.g. metal alkoxides) in organic medium;
- (ii) Via ionic precursors in aqueous medium (citrate gel process).

The purity, microstructure and physical properties of the product are controlled by varying the precursor, solvent, pH, firing temperatures and atmosphere of heat treatment.

#### 4.1. 214 Cuprates

Superconducting 214 compounds are prepared both by means of organometallic precursor [178] and by the citrate gel process [11]. Lanthanum 2,4-pentanedionate, barium 2,4-pentanedionate and copper (II) ethyl hexanoate are mixed at room temperature in the appropriate ratios in methoxyethanol medium to obtain the organometallic precursor. After vigorous stirring at room temperature, the precursor gel is converted to monophasic  $\text{La}_{1.9}\text{Ba}_{0.1}\text{CuO}_4$  ( $T_c$  23 K) by firing at 873 K in oxygen.

In the citrate gel process, a mixture of citric acid and ethylene glycol is added to the solution containing the required quantities of metal nitrates. The resulting solution is vigorously stirred and heated around 393 K. During this process, oxides of nitrogen evolve, resulting in a viscous gel. The gel is decomposed at 673 K in air and the resulting black powder is then given the necessary heat treatment to obtain the superconducting oxide.

#### 4.2. $\text{YBa}_2\text{Cu}_3\text{O}_7$

In the case of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , the alkoxide precursors are both very expensive and difficult to obtain. In addition, the solubility of copper alkoxides is very low in organic solvents and yttrium alkoxides are readily hydrolysed even by a trace of water. Despite these difficulties, superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  has been prepared using alkoxides [157, 179–181]. A simple reaction involving  $\text{Y}(\text{OCHMe}_2)_3$ ,  $\text{Ba}(\text{OCHMe}_2)_2$  and  $\text{Cu}(\text{NBu}_2)$  in THF in an argon atmosphere gives the organometallic precursor [157]. The precursor powder, after removal of the solvent, is sintered at 973 K in flowing argon to obtain tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . Following oxygenation at 673 K, the product shows a  $T_c$  of 85 K. Superconducting properties have been improved by using *n*-butoxides of Y, Ba and Cu in butanol solvent [179].

Alternatively, methoxyethoxides of yttrium, barium and copper have been used as precursors in methoxyethanol–methylethylketone–toluene solvent mixture to prepare  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  [180]. In some of the preparations,  $\text{Cu}(\text{NO}_3)_2$  (soluble in ethanol) or copper

acetylacetonate (soluble in toluene) is used along with the alkoxides of yttrium and barium to overcome the problem of low solubility of copper alkoxides [182, 183]. Organometallic precursors involving propionates [153] and neodeconates [184] have also been used for preparing  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .

Modified sol-gel methods which do not involve the metal alkoxide precursors have been employed by many workers. Thus, Nagano and Greenblatt [185] have employed metal nitrates dissolved in ethylene glycol. After refluxing around 353 K under vigorous stirring, a bluish green colloidal gel is obtained. The gel is converted into orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  by heating to 1223 K in flowing oxygen. Precipitating all the three ions as hydroxides also results in fine colloidal particles of the starting materials [186–188]. The precipitation is generally carried out by the addition of  $\text{NH}_4\text{OH}$  [186],  $\text{N}(\text{CH}_3)_4\text{OH}$  [187] or  $\text{Ba}(\text{OH})_2$  [188] to a solution of metal nitrates (pH range 7–8). These hydroxides are decomposed around 1223 K in oxygen to give  $\text{YBa}_2\text{Cu}_3\text{O}_7$  showing a  $T_c$  of 93 K.

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  has been prepared by the citrate gel process [189–193]. In this method 1 g equivalent of citric acid is added to each gram equivalent of the metal. The pH of the solution is adjusted to around 6 (either by  $\text{NH}_4\text{OH}$  or by ethylenediamine). Evaporation of the solvent (water) around 353 K, results in a viscous dark blue gel. The gel is decomposed and the powder sintered in the form of pellets at 1173 K in oxygen to obtain orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $T_c$  = 93 K). By this method, ultrafine homogeneous powders (particle size  $\sim 0.3 \mu\text{m}$ ) are obtained. The crucial step in this process is the adjustment of the pH which controls the stoichiometry of the final product. This limitation has been overcome by dispersing the citrate metal ion complexes in a solvent mixture of ethylene glycol and water [194, 195].

Problems such as the formation of  $\text{BaCO}_3$  during the calcination step, filtration and contamination of alkali metal ions in the final product are avoided in the sol-gel process. Furthermore, perfect homogeneity is obtained before calcination. The sol-gel process (e.g. citrate process) has the advantage over the other methods in that the gel can be used for making thick and thin superconducting films, fibres etc which have technological importance [179, 185, 186, 196–198].

#### 4.3. $\text{YBa}_2\text{Cu}_4\text{O}_8$

The sol-gel method offers a good alternative to the ceramic method for the synthesis of superconducting  $\text{YBa}_2\text{Cu}_4\text{O}_8$ . The following procedure has been used to prepare  $\text{YBa}_2\text{Cu}_4\text{O}_8$  at 1 atm oxygen pressure [199]. Appropriate quantities of  $\text{Y}(\text{n-OC}_4\text{H}_9)_3$ ,  $\text{Ba}(\text{s-OC}_4\text{H}_9)_2$  and  $\text{Cu}(\text{s-OBu})_2$  in butanol–xylene mixture are refluxed in an argon atmosphere at 343 K for a period of 30 h. The fine powder after the vigorous reaction is freed from the solvent and dried. The powder is heated in the form of pellets at 1033 K in flowing oxygen to obtain superconducting  $\text{YBa}_2\text{Cu}_4\text{O}_8$ .

the 124 cuprate is quite rapid.  $\text{Cu}(\text{NO}_3)_2$  has also been used as the source of copper in this procedure [200].

In the modified citrate gel process to prepare  $\text{YBa}_2\text{Cu}_4\text{O}_8$  [201, 202], 1 g equivalent of citric acid is added for each gram equivalent of the metal and the pH of the solution is adjusted to  $\sim 5.5$  by the addition of ethylenediamine. The resulting clear solution is evaporated to yield a viscous purple gel. The decomposed gel is sintered in flowing oxygen for 3–5 days at 1088 K to obtain nearly monophasic  $\text{YBa}_2\text{Cu}_4\text{O}_8$  ( $T_c = 66$  K). Kakihana *et al* [203] have reported the preparation of  $\text{YBa}_2\text{Cu}_4\text{O}_8$  using a precursor obtained from citrate metal ion complexes uniformly dispersed in a solvent mixture of ethylene glycol and water. This method yields phase-pure  $\text{YBa}_2\text{Cu}_4\text{O}_8$  ( $T_c \sim 79$  K) and eliminates the need to adjust the pH.

#### 4.4. Bismuth cuprates

There have been very few reports of the preparation of bismuth-based cuprate superconductors by the alkoxy sol-gel method [204]. Some of the difficulties arise because the relevant bismuth/lead alkoxides are not readily available; it is also not easy to get a common organic solvent to dissolve the various metal alkoxides simultaneously. Dhalle *et al* [204] have, however, attempted to synthesize the lead-doped  $n = 3$  member (2223) using organometallic precursors involving propionates. The starting materials were taken in the form of nitrates and converted into propionates by the addition of an excess of 100% propyl alcohol. This step was followed by the addition of ammonium hydroxide and ethylene glycol to increase the alkoxy anion concentration, thus in turn increasing the viscosity of the solution. All the solutions were mixed together and dried at 353 K. The resin after calcination at 1123 K in air and sintering at 1118 K gave a mixture of the  $n = 3$  and  $n = 2$  members.

A simple sol-gel method involving the addition of dilute ammonia to an aqueous solution containing nitrates of Bi, Sr and acetates of Ca, Cu and Pb (until the pH of the solution reached around 5.5) has also been employed to prepare bismuth cuprates [205, 206]. The blue solution after concentrating at around 343 K gives a viscous gel. The gel is decomposed and the powder sintered at around 1128 K in air. The product from this procedure is multiphasic showing a  $T_c$  of 104 K. The simplicity of the method and the formation of the  $n = 3$  phase in a short time makes it somewhat superior to the conventional ceramic route. The modified citrate gel process has been employed to prepare the  $n = 2$  member (2212) in pure form with a  $T_c$  of 78 K [193].

#### 4.5. Lead cuprates

The modified citrate gel process has been successfully employed by Mahesh *et al* [207] for the synthesis of lead cuprates of the 2213 or 1212 type. In a typical procedure, a mixture of citric acid and ethylene glycol in

solution of the relevant cations. The clear blue solution is concentrated at 373 K in order to get a viscous gel. The gel after decomposition is heated in the form of pellets in the temperature range of 1073–1173 K either in  $\text{N}_2$  containing 1%  $\text{O}_2$  or in an oxygen atmosphere.  $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_{8+x}$  obtained from this process shows a sharp superconducting transition at 70 K. The 1212 cuprate also shows a sharp transition at 60 K. This process is superior to the ceramic procedure for synthesizing superconducting lead cuprates.

#### 5. Alkali flux method

Strong alkaline media, either in the form of solid carbonate fluxes, molten hydroxides or highly concentrated alkali solutions can be employed for the synthesis of high- $T_c$  cuprate superconductors. The alkali flux method takes advantage of both the moderate temperatures of the molten media (453–673 K) as well as of the acid-base characteristics of molten hydroxides to simultaneously precipitate oxides or oxide precursors such as hydroxides or peroxides of the constituent metals. The method stabilizes higher oxidation states of the metal by providing an oxidizing atmosphere.

Employing fused alkali hydroxides, Ham *et al* [208] have synthesized superconducting  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  ( $\text{M} = \text{K}$  or  $\text{Na}$  or vacancy) at relatively low temperatures (470–570 K). In this method, stoichiometric quantities of  $\text{La}_2\text{O}_3$  and  $\text{CuO}$  are added to a molten mixture containing  $\text{KOH}$  and  $\text{NaOH}$  (in an approximately 1 : 1 ratio) in a Teflon crucible and heated at around 570 K in air for 100 h. The 1 : 1 mixture of  $\text{KOH}$  and  $\text{NaOH}$  melts at 440 K and since the alkali hydroxides generally contain some water, the melt is acidic and can readily dissolve oxides such as  $\text{La}_2\text{O}_3$  and  $\text{CuO}$ . The black crystals obtained from the reaction (after washing away the excess hydroxide with water) show a  $T_c$  of 35 K. Since the reaction is carried out in alkali hydroxides, incorporation of  $\text{Na}^+$  or  $\text{K}^+$  ions for  $\text{La}^{3+}$  in the lattice of  $\text{La}_2\text{CuO}_4$  cannot be ruled out. It should be noted that superconducting alkali-doped  $\text{La}_2\text{CuO}_4$  is normally prepared at higher temperatures in sealed gold tubes [209]. Recently, alkaline hypobromite oxidation has been employed to obtain  $\text{La}_2\text{CuO}_{4+x}$  with a  $T_c$  of 44 K [210].

Superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_7$  ( $T_c \sim 88$  K) has also been prepared using the fused eutectic of sodium and potassium hydroxides in a similar manner to that described above [211]. The problem of contamination of alkali metals in the preparation of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  has been overcome by using the  $\text{Ba}(\text{OH})_2$  flux [211]. The procedure involves heating a mixture containing stoichiometric amounts of  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ba}(\text{OH})_2$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in an open ceramic crucible at around 1023 K in air for a short time (about 10 min) and then slowly cooling the melt to room temperature. Since  $\text{Ba}(\text{OH})_2$  has two hydration states, one melting at 351 K and the other at 681 K, the lower-melting hydrate acts as the solvent for the nitrates of copper

and yttrium while the high-melting hydrate serves as the medium for intimate mixing of the reactants. The precipitate obtained from the melt, after washing with water, is sintered in air at around 1173 K followed by oxygenation at 773 K. This method yields an orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_7$  phase (with little  $\text{CuO}$  impurity) showing a  $T_c$  of 92 K.

The flux method eliminates the need for mechanical grinding and introduction of carbon-containing anions, which is often encountered in the solution routes. Furthermore, the method is efficient and cost-effective.

## 6. Combustion method

Although many of the solution routes discussed earlier yield homogeneous products, the processes involved are quite complex. Combustion synthesis or self-propagating high-temperature synthesis (SHS), first developed by Merzhanov and Borovinskaya [212], provides a simple and rapid means of preparing inorganic materials, many of which are technologically important. Combustion synthesis is based on the principle that the heat energy liberated by many exothermic non-catalytic solid-solid or solid-gas reactions can self-propagate throughout the sample at a certain rate. This process can therefore occur in a narrow zone which separates the starting substances and reaction products.

Self-propagating combustion has been employed recently in this laboratory to synthesize members of almost all families of cuprate superconductors (except for the thallium cuprates) [213]. The method involves the addition of an appropriate fuel to a solution containing the metal nitrates in the proper stoichiometry. The ratio of the metal nitrates to the fuel is such that when the solution is dried at around 423 K, the solid residue undergoes flash combustion, giving an ash containing the mixture of oxides in the form of very fine particles (particle size 0.3–0.5  $\mu\text{m}$ ). The ash is then given proper heat treatment under the desired atmosphere to obtain the cuprate. The small particle size of the ash facilitates the reaction between the metal oxides due to smaller diffusion distances between the cations. Fuels such as urea [213, 214], glycine [213, 215] and tetraformal triazine (TFTA) [216] are generally employed for synthesizing cuprate superconductors. Ultrafine particles of copper metal can also act as an internal fuel wherein the combustion is initiated by flashing a laser beam for a short time [217]. Some of the cuprate superconductors which have been prepared [213] by this route include  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  ( $T_c = 35$  K),  $\text{YBa}_2\text{Cu}_3\text{O}_7$  ( $T_c = 90$  K),  $\text{YBa}_2\text{Cu}_4\text{O}_8$  ( $T_c = 80$  K),  $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$  ( $T_c = 85$  K),  $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_8$  ( $T_c = 60$  K) and  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  ( $T_c \sim 30$  K).

## 7. Other methods

In addition to the various synthetic methods discussed hitherto, a few other methods such as spray drying [218–221], freeze drying [186, 222, 223], use of metallic precursors [224, 225] and electrochemical methods

[226, 227] have also been employed for the preparation of cuprate superconductors in bulk form. In spray drying, a solution containing the metallic constituents, usually in the form of nitrates, is sprayed in the form of fine droplets into a hot chamber. The solvent evaporates instantaneously, leaving behind an intimate mixture of the reactants which on heating at the desired temperature in a suitable atmosphere yields the cuprate. Some of the superconducting cuprates prepared by this method include  $\text{YBa}_2\text{Cu}_3\text{O}_7$  ( $T_c = 91$  K) [218],  $\text{YBa}_2\text{Cu}_4\text{O}_8$  ( $T_c = 81$  K) [219] and  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  ( $T_c = 101$  K) [220, 221]. In freeze drying, the reactants (in a common solvent) are frozen by immersing in liquid nitrogen. The solvent is removed at low pressures to obtain the initial reactants in fine powder form, and these are then processed at an appropriate temperature. For example,  $\text{YBa}_2\text{Cu}_3\text{O}_7$  ( $T_c = 87$  K) [186],  $\text{YBa}_2\text{Cu}_4\text{O}_8$  ( $T_c = 79$  K) [222] and  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_3\text{O}_7$  ( $T_c = 101$  K) [223] have been prepared by this method.

Metallic precursors have been used in the preparation of 123 and 247 cuprates [224, 225]. For example, oxidizing an Er–Ba–Cu alloy around 1170 K gives superconducting  $\text{ErBa}_2\text{Cu}_3\text{O}_7$  with a  $T_c$  of 87 K [224]. Similarly  $\text{Yb}_2\text{Ba}_4\text{Cu}_8\text{O}_{15}$  has been obtained by heating an alloy composition of  $\text{YbBa}_2\text{Cu}_3$  (with 33 wt% of silver) under 1 atm oxygen at 1173 K [225].

Making use of electrochemical oxidation,  $\text{La}_2\text{CuO}_{4+\delta}$  with a  $T_c$  of 44 K has been prepared at room temperature, which is otherwise possible only by use of high oxygen pressures [226, 227].

## 8. Oxygen non-stoichiometry

Oxygen stoichiometry plays a crucial role in determining the superconducting properties of many of the cuprates. Thus, stoichiometric  $\text{La}_2\text{CuO}_4$  is an insulator, while an oxygen-excess material prepared under high oxygen pressures shows superconductivity with a  $T_c$  of 35 K [15]. The same holds for the next member of the homologous family,  $\text{La}_{2-x}\text{Sr}_x\text{CaCu}_2\text{O}_6$  which is superconducting only when there is an oxygen excess [17]. The excess oxygen donates holes in these two systems. In the case of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , oxygen can be easily removed giving rise to tetragonal non-superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_6$ . The  $\text{YBa}_2\text{Cu}_3\text{O}_6$  material can be prepared by heating  $\text{YBa}_2\text{Cu}_3\text{O}_7$  in an argon atmosphere at 973 K for extended periods of time [228]. The variation of  $T_c$  with oxygen stoichiometry,  $\delta$ , is well known [229, 230]. When  $\delta$  reaches 0.5, there is an intergrowth of  $\text{YBa}_2\text{Cu}_3\text{O}_6$  and  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and at this composition, the material shows a  $T_c$  of 45 K. The  $\delta = 0.5$  composition is obtained by quenching  $\delta \approx 0$  material, heated in a nitrogen atmosphere at 743 K [231]. Similarly, by quenching  $\text{YBa}_2\text{Cu}_3\text{O}_7$  at 783 K in air,  $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$  (showing a  $T_c$  of  $\sim 60$  K) is prepared [231]. The  $T_c$  of 90 K is found only when  $\delta \leq 0.2$ .  $\text{YBa}_2\text{Cu}_3\text{O}_6$  is readily oxidized back to  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . It may be noted that this oxidation-reduction process in

Table 6. Recommended synthetic methods for selected cuprate superconductors.

Cuprate	$T_c$ (K) (approx.)	Methods of synthesis*
$\text{La}_{2-x}\text{Sr}_x(\text{Ba})\text{CuO}_4$	35	Ceramic*, sol-gel, combustion, coprecipitation
$\text{La}_2\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_2\text{O}_6$	60	Ceramic (high $\text{O}_2$ pressure)*
$\text{La}_2\text{CuO}_{4+\delta}$	40	Ceramic (high $\text{O}_2$ pressure)* alkali-flux, hypobromite*
$\text{YBa}_2\text{Cu}_3\text{O}_7$ <sup>b</sup>	90	Ceramic (annealing in $\text{O}_2$ )*, sol-gel*, coprecipitation*, combustion
$\text{YBa}_2\text{Cu}_4\text{O}_8$ <sup>b</sup>	80	Ceramic (high $\text{O}_2$ pressure), ceramic (with $\text{Na}_2\text{O}_2$ )* sol-gel*, coprecipitation*
$\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$	90	Ceramic (air-quench)* sol-gel*, combustion, melt (glass) route*
$\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}$	110	Ceramic*, sol-gel, melt route
$\text{TlCaBa}_2\text{Cu}_2\text{O}_{8+\delta}$ <sup>c</sup>	90	Ceramic (sealed Ag/Au tube)*
$\text{TlCa}_2\text{Ba}_2\text{Cu}_3\text{O}_{8+\delta}$ <sup>c</sup>	115	Ceramic (sealed Ag/Au tube)*
$\text{Tl}_2\text{Ba}_2\text{CuO}_6$ <sup>c</sup>	90	Ceramic (sealed Ag/Au tube)*
$\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$	110	Ceramic (sealed Ag/Au tube)*
$\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$	125	Ceramic (sealed Ag/Au tube)*
$\text{Tl}_{0.5}\text{Pb}_{0.5}\text{CaSr}_2\text{Cu}_2\text{O}_{8+\delta}$	90	Ceramic (sealed Ag/Au tube)*
$\text{Pb}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_3\text{O}_8$	70	Ceramic (low $\text{O}_2$ partial pressure)*, sol-gel* (low $\text{O}_2$ partial pressure)
$\text{Pb}_{0.5}\text{Cu}_{0.5}\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_7$	45	Ceramic (flowing $\text{O}_2$ )*
$\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$	30	Ceramic (low $\text{O}_2$ partial pressure)*
		Coprecipitation (low $\text{O}_2$ partial pressure)*
$\text{Ca}_{1-x}\text{Sr}_x\text{CuO}_2$	40–110	Ceramic (high pressures)*
$\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$	40–110	Ceramic (high pressures)*

\* Recommended methods are indicated by asterisks.

<sup>b</sup> Other rare-earth compounds of this type are also prepared by similar methods. Oxygen annealing is done below the orthorhombic-tetragonal transition.

<sup>c</sup> Sr analogues of these compounds with different substitutions at Ca and Tl sites are prepared by a similar procedure.

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is of topochemical character. The other analogous rare-earth 123 cuprates also behave in a similar way with respect to the variation of  $\delta$  with  $T_c$  [232].

While  $\text{YBa}_2\text{Cu}_4\text{O}_8$  has high oxygen stability,  $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15-\delta}$  shows a wide range of oxygen stoichiometry ( $0 \leq \delta \leq 1$ ) [233]. The maximum  $T_c$  of 90 K is achieved when  $\delta$  is close to zero, and when  $\delta$  reaches unity the material shows a  $T_c$  of 30 K; there is no structural phase transition accompanying the variation in oxygen stoichiometry. Usually, both yttrium 124 and 247 cuprates and their rare-earth analogues, prepared by the ceramic method under 1 atm oxygen pressure, show  $\delta$  close to zero.

Bismuth cuprates of the type  $\text{Bi}_2(\text{Ca}, \text{Sr})_{n+1}\text{Cu}_n\text{O}_{2n+4+\delta}$  are best prepared by quenching the samples in air or by annealing in a nitrogen atmosphere at appropriate temperatures [53, 234]. Heating the samples in an oxygen atmosphere is no good, possibly because the extra oxygen may add on to the Bi-O layers. In the case of the lead-doped  $n = 3$  member (2223), preparing the samples under low partial pressures of oxygen is found to increase the volume fraction of the superconducting phase [235, 236]. The  $n = 1$  member,  $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta}$  shows metallic behaviour when there is excess oxygen [237]. By annealing in a reducing atmosphere (Ar or  $\text{N}_2$ ), the excess oxygen can be removed to induce superconductivity.

Oxygen stoichiometry has a dramatic influence on the superconducting properties of thallium cuprates [94, 108, 109, 238–246]. For example, thallium cuprates of the  $\text{TlCa}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+3}$  family, derivatives of the

$\text{TlCa}_{n-1}\text{Sr}_2\text{Cu}_n\text{O}_{2n+3}$  family and  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$  often have excess oxygen when prepared in sealed tubes. By annealing these samples in a reducing atmosphere (Ar, dilute  $\text{H}_2$ ,  $\text{N}_2$  or vacuum) at appropriate temperatures, the excess oxygen is removed to induce superconductivity in some cases [108, 109, 238]. Annealing at low oxygen partial pressures or in a reducing atmosphere also increases the  $T_c$  of some of the superconducting thallium cuprates to higher values by decreasing the oxygen content [94, 239–246]. These variations are clearly related to the hole concentration where the number of holes decreases by removing excess oxygen, thereby giving the optimal concentration required for maximal  $T_c$  [247].

In lead cuprates of the  $\text{Pb}_2\text{Sr}_2(\text{Ln}, \text{Ca})\text{Cu}_3\text{O}_{8+\delta}$  (2213) type, increasing the oxygen content of the material by annealing in an oxygen atmosphere oxidizes the  $\text{Pb}^{2+}$  and  $\text{Cu}^{1+}$  without affecting the  $\text{CuO}_2$  sheets, which governs the superconductivity in this material [248]. Though this system shows a wide range of oxygen stoichiometry (associated with a structural phase transition from orthorhombic to tetragonal symmetry), maximum  $T_c$  is observed for any given composition where in  $\delta$  is close to zero [249]. Samples with  $\delta \approx 0$  are therefore prepared by annealing in a nitrogen atmosphere containing little oxygen. The lead 1212 cuprates, on the other hand, are best prepared in a flowing oxygen atmosphere. The samples obtained after the oxygen treatment are often not superconducting since there is an oxygen excess. The samples are quenched in air at around 1073 K in order to achieve superconductivity [250].



Superconducting properties of the electron-doped superconductors,  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ , are sensitive to the oxygen content. The as-prepared samples which are semiconducting have oxygen content greater than four. Samples with oxygen content less than four are obtained by annealing in a reducing atmosphere ( $\text{N}_2$ , Ar or dilute  $\text{H}_2$ ) at around 1173 K. Maintaining the oxygen stoichiometry at less than four is essential for having an oxidation state of Cu less than 2+ in this material [251].

## 9. Concluding remarks

In the earlier sections we presented details of the preparative methods for the synthesis of various families of cuprate superconductors. In addition, we also examined the advantages and disadvantages of the different methods. Since more than one method of synthesis has been employed for preparing any given cuprate, it becomes necessary to make the right choice of method in any given situation. In order to assist in making such a choice, we have tabulated in table 6 the important preparative methods employed to synthesize some of the representative cuprates, where the recommended methods are also indicated.

## Acknowledgment

The authors thank the various agencies, especially the National Superconductivity Research Board, University Grants Commission and the US National Science Foundation for support of the research related to cuprate superconductors.

## References

- [1] Bednorz J G and Müller K A 1986 *Z. Phys.* B **64** 189
- [2] Sleight A W 1988 *Science* **242** 1519
- [3] Rao C N R (ed) 1991 *Chemistry of High Temperature Superconductors* (Singapore: World Scientific)
- [4] Rao C N R 1991 *Phil. Trans. R. Soc. A* **336** 595
- [5] Rao C N R and Gopalakrishnan J 1989 *New Directions in Solid State Chemistry* (Cambridge: Cambridge University Press)
- [6] Rao C N R 1992 *Mater. Sci. Eng.* at press
- [7] Uchida S, Takagi H, Kitazawa K and Tanaka S 1987 *Japan. J. Appl. Phys.* **26** L1
- [8] Cava R J, Vandover R B, Batlogg B and Rietman E A 1987 *Phys. Rev. Lett.* **58** 408
- [9] Ganguly P, Mohan Ram R A, Sreedhar K and Rao C N R 1987 *Solid State Commun.* **62** 807
- [10] Tarascon J M, Greene L H, Mckinnon W R, Hull G W and Geballe T H 1987 *Science* **235** 1373
- [11] Wang H *et al* 1987 *Inorg. Chem.* **26** 1474
- [12] Bhat V, Ganguli A K, Nanjundaswamy K S, Mohan Ram R A, Gopalakrishnan J and Rao C N R 1987 *Phase Transitions* **10** 87
- [13] Kaplan M L and Hauser J J 1988 *Mater. Res. Bull.* **23** 287
- [14] Demazeau G, Trese F, Plante Th F, Chevalier B, Etorneau J, Michel C, Hervieu M, Raveau B, Lejay P, Sulpice A and Tournier T 1988 *Physica C* **153-155** 824
- [15] Schriber E, Morosin B, Merriell R M, Heava P F, Venturini E L, Kurak J F, Nigney P J, Baughman R J and Ginley D S 1988 *Physica C* **152** 121
- [16] Zhou J, Sinha S and Goodenough J B 1989 *Phys. Rev. B* **39** 12331
- [17] Cava R J, Batlogg B, Vandover R B, Krajewski J J, Waszczak J V, Flemming R M, Peck W Jr, Rupp L W Jr, Marsh P, James A C W P and Schneemeyer L F 1990 *Nature* **345** 6026
- [18] Kinoshita K, Shibata H and Yamada T 1991 *Physica C* **176** 433
- [19] Okai B 1991 *Japan. J. Appl. Phys.* **30** L179
- [20] Cava R J, Batlogg B, Vandover R B, Murphy D W, Sunshine S, Siegrist T, Rameika J P, Rietman E A, Zahurak S and Espinosa G P 1987 *Phys. Rev. Lett.* **58** 1676
- [21] Rao C N R, Ganguly P, Raychaudhuri A K, Mohan Ram R A and Sreedhar K 1987 *Nature* **326** 856
- [22] Leskela M, Mueller C H, Truman J K and Holloway P H 1988 *Mater. Res. Bull.* **23** 1469; Hepp A F and Gaier J R 1988 *Mater. Res. Bull.* **23** 693
- [23] Rao C N R 1988 *J. Solid State Chem.* **74** 147
- [24] Clarke D R 1987 *Int. J. Mod. Phys. B* **1** 170
- [25] Umarji A M and Nanjundaswamy K S 1987 *Pramana-J. Phys.* **29** L611
- [26] Tarascon J M, Mckinnon W R, Greene L H, Hull L W and Vogel E M 1987 *Phys. Rev. B* **36** 226
- [27] Alario-Franco M A, Moran-Miguel E, Saez-Puche R, Garcia-Alvarado F, Amador U, Barabona M, Fernandez F, Perez-Frias M T and Vincent J L 1988 *Mater. Res. Bull.* **23** 313
- [28] Manthiram A, Lee S J and Goodenough J B 1988 *J. Solid State Chem.* **73** 278
- [29] Cava R J, Batlogg B, Flemming R M, Sunshine S A, Ramirez A, Rietman E A, Zahurak S M and Vandover R B 1988 *Phys. Rev. B* **37** 5912
- [30] Somasundaram P, Nanjundaswamy K S, Umarji A M and Rao C N R 1988 *Mater. Res. Bull.* **23** 1139
- [31] Veal B M, Kwok W K, Umezawa A, Crabtree G W, Jorgensen J D, Downey J W, Nowicki L J, Mitchell A W, Paulikas A P and Sowers C H 1987 *Appl. Phys. Lett.* **51** 279
- [32] Tarascon J M, Barbour P, Miceli P F, Greene L H, Hull G W, Eibschutz M and Sunshine S A 1988 *Phys. Rev. B* **37** 7458
- [33] Xu Y, Sabatini R L, Moodenbaugh A R, Zhu Y, Shyu S G, Suenaga M, Dennis K W and McCallum R W 1990 *Physica C* **169** 205
- [34] Karpinski J, Kalds E, Jilek E, Rusiecki S and Bucher B 1988 *Nature* **336** 660
- [35] Cava R J, Krajewski J J, Peck W F Jr, Batlogg B, Rupp L W Jr, Fleming R M, James A C W P and Marsh P 1989 *Nature* **338** 328
- [36] Pooke D M, Buckley R G, Presland M R and Tallon J L 1990 *Phys. Rev. B* **41** 6616
- [37] Hurng W M, Wu S F and Lee W H 1990 *Solid State Commun.* **76** 647
- [38] Rao C N R, Subbanna G N, Nagarajan R, Ganguli A K, Ganapathi L, Vijayaraghavan R, Bhat S V and Raju A R 1990 *J. Solid State Chem.* **88** 163
- [39] Jin S, O'Bryan, Gallagher P K, Tiefel T H, Cava R J, Fastnacht R A and Kammlott G W 1990 *Physica C* **165** 415
- [40] Adachi S, Adachi H, Setsune K and Wasa K 1991 *Physica C* **175** 523
- [41] Buckley R G, Tallon J L, Pooke D M and Presland M R 1990 *Physica C* **165** 391
- [42] Buckley R G, Pooke D M, Tallon J L, Presland M R, Flower N E, Staines M P, Johnson H L, Meylan M, Williams G V M and Bowden M 1991 *Physica C* **174** 383

- [43] Karpinski J, Kusicki S, Kaldis E, et al and Juck L 1989 *Physica C* 160 449
- [44] Tallon J L and Lusk J 1990 *Physica C* 167 236
- [45] Morris D E, Nickel J H, Wei J Y T, Asmar N G, Scott J S, Scheven U M, Hultgren C T, Markelz A G, Post J E, Heaney P J, Veblen D R and Hazen R M 1989 *Phys. Rev. B* 39 7347
- [46] Miyatake T, Gotoh S, Koshizuka N and Tanaka S 1989 *Nature* 341 41
- [47] Wada T, Sakurai T, Suzuki N, Koriyama S, Yamauchi H and Tanaka S 1990 *Phys. Rev. B* 41 11209
- [48] Morris D E, Marathe A P and Sinha A P B 1990 *Physica C* 169 386
- [49] Bordet P, Chaillout C, Chevanas J, Hoveau J L, Marezio M, Karpinski J and Kaldis E 1988 *Nature* 334 596
- [50] Morris D E, Asmar N G, Wei J Y T, Sid R L, Nickel J H, Scott J S and Post J E 1989 *Physica C* 162-164 955
- [51] Michel C, Hervieu M, Borel M M, Grandin A, Deslandes F, Provost J and Raveau B 1987 *Z. Phys.* B 68 421
- [52] Maeda H, Tanaka Y, Fukutomi M and Asano T 1988 *Japan. J. Appl. Phys.* 27 L209
- [53] Rao C N R, Ganapathi L, Vijayaraghavan R, Ranga Rao G, Kumari Murthy and Mohan Ram R A 1988 *Physica C* 156 827
- [54] Sastry P V P S S, Gopalakrishnan I K, Sequeira A, Rajagopal H, Gangadharan K, Phatak G M and Iyer R M 1988 *Physica C* 156 230
- [55] Sastry P V P S S, Yakhmi J V and Iyer R M 1989 *Physica C* 161 656
- [56] Wang Z, Statt B W, Lee M J G, Bagheri S and Rutter J 1991 *J. Mater. Res.* 6 1160
- [57] Torrance J B, Tokura Y, LaPlaca S J, Huang T C, Savoy R J and Nazzari A I 1988 *Solid State Commun.* 66 703
- [58] Tallon J L, Buckley R G, Presland M R, Gilberd P W, Brown I W M, Bowden M and Goguel R 1989 *Phase Transitions* 19 171
- [59] Garcia-Alvarado F, Moran E, Alario-Franco M A, Gonzalez M A, Vincent J L, Cheetham A K and Chippindale A M 1990 *J. Less Common. Metals* 164-165 643
- [60] Ikeda Y, Ito H, Shimomura S, Oue Y, Inaba K, Hiroi Z and Takano M 1989 *Physica C* 159 93
- [61] Maeda A, Hase M, Tsukada I, Noda K, Takebayashi S and Uchinokura K 1990 *Phys. Rev. B* 41 6418
- [62] Sinclair D C, Irvine J T S and West A R 1992 *J. Mater. Chem.* 2 579
- [63] Agostinelli E, Bohandy J, Green W J, Phillips T E, Kim B F, Adrian F J and Moorjani K 1989 *J. Mater. Res.* 4 1103
- [64] Ganapathi L, Sujata Krishna, Kumari Murthy, Vijayaraghavan R and Rao C N R 1988 *Solid State Commun.* 67 967; Statt B W, Wang Z, Lee M J G, Yakhmi J V, Decamargo P C, Major J F and Rutter J W 1988 *Physica C* 156 251
- [65] Balachandran U, Shi D, Dos Santos D I, Graham S W, Patel M A, Tani B, Vandervoort K, Claus H and Poeppel R B 1988 *Physica C* 156 649
- [66] Green S M, Jiang C, Mei Y, Luo H L and Politis C 1988 *Phys. Rev. B* 38 5016
- [67] Varma K B R, Rao K J and Rao C N R 1989 *Appl. Phys. Lett.* 54 69
- [68] Komatsu T, Sato R, Hirose C, Matusita K and Yamashita T 1988 *Japan. J. Appl. Phys.* 27 L2293
- [69] Pandey D, Mahesh R, Singh A K, Tiwari V S and Kak S K 1991 *Physica C* 184 135
- [70] Bloom I, Frommelt J M, Hash M C, Lanagan M T, Gruber C S, György E M, Gallagher P K, O'Bryan H M, Johnson B W, Sunshine S, Zaburak S M, Jin S and Sherwood R C 1988 *Phys. Rev. B* 38 757
- [71] Shi F, Rong T S, Zhou S Z, Wu X F, Du J, Shi Z H, Cui C G, Jin R Y, Zhang J L, Ran Q Z and Shi N C 1990 *Phys. Rev. B* 41 6541
- [72] Rao C N R, Mohan Ram R A, Ganapathi L and Vijayaraghavan R 1988 *Pramana-J. Phys.* 30 L495
- [73] Zandbergen H W, Huang Y K, Menken M J V, Li J N, Kadowaki K, Menovsky A A, Van Tendeloo G and Amelinckx S 1988 *Nature* 332 620
- [74] Rao C N R, Vijayaraghavan R, Ganapathi L and Bhat S V 1989 *J. Solid State Chem.* 79 177; Losch S, Budin H, Eibl O, Hartmann M, Rentschler T, Rygula M, Kemmler-Sack S and Heubener R P 1991 *Physica C* 177 271
- [75] Darriet J, Soethout C J P, Chevalier B and Etourneau J E 1989 *Solid State Commun.* 69 1093
- [76] Manivannan V, Gopalakrishnan J and Rao C N R 1991 *Phys. Rev. B* 43 8686
- [77] Rao C N R, Nagarajan R, Vijayaraghavan R, Vasanthacharya N Y, Kulkarni G U, Ranga Rao G, Umarji A M, Somasundaram P, Subbanna G N, Raju A R, Sood A K and Chandrabhas N 1990 *Supercond. Sci. Technol.* 3 242
- [78] Manthiram A and Goodenough J B 1988 *Appl. Phys. Lett.* 53 420
- [79] Xiang X D, McKernan S, Vareka W A, Zettl A, Corkill J L, Barbee T W III and Cohen M L 1990 *Nature* 348 145
- [80] Tokura Y, Arima T, Takagi H, Uchida S, Ishigaki T, Asano H, Beyers R, Nazzari A I, Laccorre P and Torrance J B 1989 *Nature* 342 890
- [81] Remschnig K, Tarascon J M, Ramesh R, Hull G W and Rogl P 1990 *Physica C* 170 284
- [82] Arima T, Tokura Y, Takagi H, Uchida S, Beyers R and Torrance J B 1990 *Physica C* 168 79
- [83] Sequeira A, Rajagopal H, Ganapathi L, Vijayaraghavan R and Rao C N R 1989 *Int. J. Mod. Phys.* 3 445; Lee P, Gao Y, Sheu H S, Petriček V, Restori R, Coppens P, Darovskikh A, Phillips J C, Sleight A W and Subramanian M A 1989 *Science* 244 62
- [84] Cheetham A K, Chippindale A M, Hibble S J and Woodley C J 1989 *Phase Transitions* 19 223
- [85] Sheng Z Z and Hermann A M 1988 *Nature* 332 55, 138
- [86] Shimakawa Y, Kubo Y, Manoko T, Nakabayashi Y and Igarashi H 1988 *Physica C* 156 97
- [87] Torardi C C, Subramanian M A, Gopalakrishnan J, McCarron E M, Calabrese J C, Morrissey K J, Askew T R, Flippens R B, Chowdhry U, Sleight A W and Cox D E 1988 *High Temperature Superconductivity* (ed R M Metzger) (New York: Gordon and Breach) p 117
- [88] Vijayaraghavan R, Rangavittal N, Kulkarni G U, Grantscharova E, Guru Row T N and Rao C N R 1991 *Physica C* 179 183
- [89] Goretta K C, Chen J G, Chen N, Hash M O and Shi D 1990 *Mater. Res. Bull.* 25 791
- [90] Schilling A, Ott H R and Hulliger F 1989 *Physica C* 157 144
- [91] Rao C N R, Ganguli A K and Vijayaraghavan R 1989 *Phys. Rev. B* 40 2505; Ganguli A K, Vijayaraghavan R and Rao C N R 1989 *Phase Transitions* 19 213
- [92] Parkin S S P, Lee V Y, Nazzari A I, Savoy R, Huang T C, Gorman G and Beyers R 1988 *Phys. Rev. B* 38 6531
- [93] Martin C, Maignan A, Provost J, Michel C, Hervieu M, Tournier R and Raveau B 1990 *Physica C* 168 8

- [95] Barry J C, Iqbal Z, Ramakrishna B L, Sharma R, Eckhardt H and Reidinger F 1989 *J. Appl. Phys.* **65** 5207
- [96] Gopalakrishnan I K, Sastry P V P S S, Gangadharan K, Phatak G M, Yakhmi J V and Iyer R M 1988 *Appl. Phys. Lett.* **53** 414
- [97] Li S and Greenblatt M 1989 *Physica C* **157** 365
- [98] Ganguli A K, Nanjundaswamy K S, Subbanna G N, Rajumon M K, Sarma D D and Rao C N R 1988 *Mod. Phys. Lett. B* **2** 1169
- [99] Sleight A W 1991 *Phys. Today* **44** 24
- [100] Parkin S S P, Lee V Y, Engler E M, Nazzari A I, Huang T C, Gorman G, Savoy R and Beyers R 1988 *Phys. Rev. Lett.* **60** 2539
- [101] Vijayaraghavan R, Gopalakrishnan J and Rao C N R 1992 *J. Mater. Chem.* **2** 237
- [102] Suigse R, Herbayashi M, Terada N, Jo M, Shimomura T and Ihara H 1988 *Japan. J. Appl. Phys.* **27** 1709
- [103] Suigse R, Herbayashi M, Terada N, Jo M, Shimomura T and Ihara H 1989 *Physica C* **157** 131
- [104] Ganguli A K, Nanjundaswamy K S and Rao C N R 1988 *Physica C* **156** 788
- [105] Subramanian M A, Torardi C C, Gopalakrishnan J, Gai P L, Calabrese J C, Askew T R, Flippen R B and Sleight A W 1988 *Science* **242** 249
- [106] Subramanian M A, Gai P L and Sleight A W 1990 *Mater. Res. Bull.* **25** 101
- [107] Pan M H and Greenblatt M 1991 *Physica C* **176** 80
- [108] Pan M H and Greenblatt M 1991 *Physica C* **184** 235
- [109] Ganguli A K, Manivannan V, Sood A K and Rao C N R 1989 *Appl. Phys. Lett.* **55** 2664
- [110] Manivannan V, Ganguli A K, Subbanna G N and Rao C N R 1990 *Solid State Commun.* **74** 87
- [111] Manako T, Shimakawa Y, Kubo Y, Satoh T and Igarashi H 1989 *Physica C* **158** 143
- [112] Martin C, Bourgault D, Hervieu M, Michel C, Provost J and Raveau B 1989 *Mod. Phys. Lett. B* **3** 993
- [113] Vijayaraghavan R 1992 *PhD Thesis* Indian Institute of Science
- [114] Liu R S, Hervieu M, Michel C, Maignan A, Martin C, Raveau B and Edwards P P 1992 *Physica C* **197** 131
- [115] Torardi C C, Subramanian M A, Calabrese J C, Gopalakrishnan J, Morrissey K J, Askew T R, Flippen R B, Chowdhry U and Sleight A W 1988 *Science* **240** 631
- [116] Cava R J *et al* 1988 *Nature* **336** 211
- [117] Koike Y, Masuzawa M, Noji T, Sunagawa H, Kawabe H, Kobayashi N and Saito Y 1990 *Physica C* **170** 130
- [118] Subramanian M A, Gopalakrishnan J, Torardi C C, Gai P L, Boyes E D, Askew T R, Flippen R B, Farneth W E and Sleight A W 1989 *Physica C* **157** 124
- [119] Kadowaki K, Menken M J V and Moleman A C 1989 *Physica C* **159** 165
- [120] Ramprasad, Soni N C, Adhikary K, Malik S K and Tomy C V 1990 *Solid State Commun.* **76** 667
- [121] Retoux R, Michel C, Hervieu M and Raveau B 1989 *Mod. Phys. Lett. B* **3** 591
- [122] Zandbergen H W, Fu W T, Van Ruitenbeck J M and Amelinckx S 1989 *Physica C* **159** 81
- [123] Adachi S, Setsune K and Wasa K 1990 *Japan. J. Appl. Phys.* **29** L890
- [124] Maeda T, Sakuyama K, Koriyama S, Yamauchi H and Tanaka S 1991 *Phys. Rev. B* **43** 7866
- [125] Rouillon T, Provost J, Hervieu M, Groult D, Michel C and Raveau B 1989 *Physica C* **159** 201
- [126] Rouillon T, Maignan A, Hervieu M, Michel C, Groult D and Raveau B 1990 *Physica C* **171** 7
- [127] Liu R S, Wu S F, Gameson I, Edwards P P, Maignan A, Rouillon T, Groult D and Raveau B 1991 *J. Solid State Chem.* **93** 276
- [128] Mohan Ram R A and Clearfield A 1991 *Chem. Mater.* **3** 313
- [129] Maeda T, Sakuyama K, Koriyama S, Ichinose A, Yamauchi H and Tanaka S 1990 *Physica C* **169** 133
- [130] Tang X X, Morris D E and Sinha A P B 1991 *Phys. Rev. B* **43** 7936
- [131] Liu H B and Morris D E 1991 *Phys. Rev. B* **44** 5369
- [132] Tokura Y, Takagi H and Uchida S 1989 *Nature* **337** 345
- [133] Markert J T and Maple M B 1989 *Solid State Commun.* **70** 145
- [134] Markert J T, Early E A, Bjornholm T, Ghanaty S, Lee B W, Neumier J J, Price R D, Seaman C L and Maple M B 1989 *Physica C* **159** 178
- [135] Lopez-Morales M E, Savoy R J and Grant P M 1990 *J. Mater. Res.* **5** 2041
- [136] James A C W P, Zahurak S M and Murphy D W 1989 *Nature* **338** 240
- [137] Felner I, Yaron U, Yeshurun Y, Yacoby E R and Wolfus Y 1989 *Phys. Rev. B* **40** 11366
- [138] Ayoub N Y, Almasan C C, Early E A, Markert J T, Seaman C L and Maple M B 1990 *Physica C* **170** 211
- [139] Takano M, Azuma M, Hiroi Z, Bando Y and Takeda Y 1991 *Physica C* **176** 441
- [140] Takano M, Hiroi Z, Azuma M and Takeda Y 1992 *Chemistry of High Temperature Superconductors* (ed C N R Rao) (Singapore: World Scientific) p 243
- [141] Smith M G, Manthiram A, Zhou J, Goodenough J B and Markert J T 1991 *Nature* **351** 549
- [142] Azuma M, Hiroi Z, Takano M, Bando Y and Takeda Y 1992 *Nature* **356** 775
- [143] Capone D W, Hinks D G, Jorgensen J D and Zhang Z K 1987 *Appl. Phys. Lett.* **50** 543
- [144] Bednorz J G, Takashige M and Müller K A 1987 *Mater. Res. Bull.* **22** 819
- [145] Jorgensen J D, Schuttler H B, Hinks D G, Capone D W, Zhang K, Brodsky M B and Scalapino D 1987 *Phys. Rev. Lett.* **58** 1024
- [146] Otamiri J C and Anderson A 1990 *J. Mater. Res.* **5** 1388
- [147] Panayappan R M, Guy J T, Binstead R, Toysneau V L and Cooper J C 1988 *Phys. Rev. B* **37** 3727
- [148] McIntyre P C, Cima M J, Man Fai Ng, Chiu R C and Rhine W E 1990 *J. Mater. Res.* **5** 2771
- [149] Manthiram A and Goodenough J B 1987 *Nature* **329** 701
- [150] Wang X Z, Henry M, Livage J and Rosenmann I 1987 *Solid State Commun.* **64** 881
- [151] Clark R J, Harrison L L, Skirius S A and Wallace W J 1990 *Mol. Cryst. Liq. Cryst.* **184** 377
- [152] Vos A, Carleer R, Mullens J, Yperman J, Vanhees J and Van Poucke L C 1991 *Eur. J. Solid State Inorg. Chem.* **28** 657
- [153] Vilminot S, Hadigui S El and Desory A 1988 *Mater. Res. Bull.* **23** 521
- [154] Pramanik P, Biswas S, Singh C, Bhattacharya D, Dey T K, Sen D, Ghatak S K and Chopra K L 1988 *Mater. Res. Bull.* **23** 1693
- [155] Kellner K, Wang X Z, Gritzner G and Bauvale D 1991 *Physica C* **173** 208
- [156] Liu R S, Chang C T and Wu P T 1989 *Inorg. Chem.* **28** 154
- [157] Horowitz H S, McIn S J, Sleight A W, Druliner J D, Gai P L, Van Kavelaar M J, Wagner J L, Biggs B D and Poon S J 1989 *Science* **243** 66
- [158] Kini A M, Geiser U, Kao H C I, Carlson D K, Wang H H, Monaghan M R and Williams J M 1987 *Inorg. Chem.* **26** 1834



- [159] D C 1990 *Mater. Res. Bull.* 25
- [160] Ho J S, Liu R S, Chang C T and Edwards P P 1991 *J. Chem. Soc. Chem. Commun.* 664
- [161] Chen W L, Huang Y, Wu M K, Wang M J, Chen D H, Sheen S R and Chang C T 1991 *Physica C* 185-189 483
- [162] Guptasarma P, Palkar V R and Multani M R 1991 *Solid State Commun.* 77 769
- [163] Liu R S, Ho J S, Chang C T and Edwards P P 1991 *J. Solid State Chem.* 92 247
- [164] Das Santos D I, Balachandran U, Gutschow R A and Poeppel R B 1990 *J. Non-Cryst. Solids* 121 441
- [165] Zhang Y, Fang Z, Muhammed M, Rao K V, Skumryev V, Medelihu H and Costa J L 1989 *Physica C* 157 108
- [166] Marbach G, Stotz S, Klee M and Devries J W C 1989 *Physica C* 161 111
- [167] Takano M, Takada J, Oda K, Kitaguchi H, Miura Y, Ikeda Y, Tomi Y and Mazaki H 1988 *Japan. J. Appl. Phys.* 27 L1041
- [168] Chen F H, Hoo K S and Tseng T Y 1990 *J. Mater. Sci.* 25 3338
- [169] Hagberg J, Vusimaki A, Levoska J and Leppavuori S 1989 *Physica C* 160 369
- [170] Gritzner G and Bernhard K 1991 *Physica C* 181 201
- [171] Chiang C, Shie C Y, Huang Y T, Lee W H and Wu P T 1990 *Physica C* 170 383
- [172] Chen D Y, Shei C Y, Sheen S R and Chang C T 1991 *Japan. J. Appl. Phys.* 30 1198
- [173] Shei C Y, Liu R S, Chang C T and Wu P T 1990 *Inorg. Chem.* 29 3117
- [174] Bernhard K, Gritzner G, Wang X Z and Bauerle D 1990 *J. Solid State Chem.* 86 293
- [175] Schrodtt D J et al 1988 *Solid State Commun.* 67 871
- [176] Borik M, Chernikov M, Dubov I, Osiko V, Veselago V, Yakowets Y and Stepankin V 1992 *Supercond. Sci. Technol.* 5 151
- [177] Bernhard K and Gritzner G 1992 *Physica C* 196 259
- [178] Kordas G, Wu K, Brahme U S, Friedmann T A and Ginsberg D M 1987 *Mater. Lett.* 5 417
- [179] Shibata S, Kitagawa T, Okazaki H, Kimura T and Murakami T 1988 *Japan. J. Appl. Phys.* 27 L53
- [180] Kordas G, Moore G A, Jorgensen J D, Rotella F, Hitterman R L, Volin K J and Faber J 1991 *J. Mater. Chem.* 1 175
- [181] Katayama S and Sekine M 1990 *J. Mater. Res.* 5 683
- [182] Murakami H, Yaegashi S, Nishino J, Shiohara Y and Tanaka S 1990 *Japan. J. Appl. Phys.* 29 2715
- [183] Catania P, Hovnanian N, Cot L, Pham Thi M, Kormann R and Ganne J P 1990 *Mater. Res. Bull.* 25 631
- [184] Bowmer T N and Shokoohi F K 1991 *J. Mater. Res.* 6 670
- [185] Nagano M and Greenblatt M 1988 *Solid State Commun.* 67 595
- [186] Barboux P, Tarascon J M, Greene L H, Hull G W and Bagley B G 1988 *J. Appl. Phys.* 63 2725
- [187] Fujiki M, Hikita M and Sukegawa K 1987 *Japan. J. Appl. Phys.* 26 L1159
- [188] Karis T E and Economy J 1991 *J. Mater. Res.* 6 1623
- [189] Chu C T and Dunn B 1987 *J. Am. Ceram. Soc.* 70 C375
- [190] Blank D H A, Kruidhof H K and Flokstra J 1988 *J. Phys. D: Appl. Phys.* 21 226
- [191] Sanjines R, Ravindranathan Thampi K and Kiwi J 1988 *J. Am. Ceram. Soc.* 71 512
- [192] Yang Y M, Out P, Zhao B R, Zhao Y Y, Li L, Ran Q Z and Jin R Y 1989 *J. Appl. Phys.* 66 312
- [193] Liu R S, Wang W N, Chang C T and Wu P T 1989 *Japan. J. Appl. Phys.* 28 L2155
- [194] Lee H K, Kim D and Sucks S I 1989 *J. Appl. Phys.* 65 2563
- and Norling P *Physica C* 162-164 931
- [196] Katayama S and Sekine M 1991 *J. Mater. Res.* 6 1629; 1991 *J. Mater. Chem.* 1 1031
- [197] Zhang S C, Messing G L, Huebner W and Coleman M M 1990 *J. Mater. Res.* 5 1806
- [198] Sakka S, Kozuka H and Zhuang H 1990 *Mol. Cryst. Liq. Cryst.* 184 359
- [199] Koriyama S, Ikemachi T, Kawano T, Yamauchi H and Tanaka S 1991 *Physica C* 185-189 519
- [200] Murakami H, Yaegashi Y, Nishino J, Shiohara Y and Tanaka S 1990 *Japan. J. Appl. Phys.* 29 L445
- [201] Liu R S, Jones R, Bennett M J and Edwards P P 1990 *Appl. Phys. Lett.* 57 920
- [202] Koyama K, Junod A, Graf T, Triscone G and Muller J 1991 *Physica C* 185-189 461
- [203] Kakihana M, Kall M, Borjesson L, Mazaki H, Yasuoka H, Berastegui P, Eriksson S and Johansson L G 1991 *Physica C* 173 377
- [204] Dhalle M, Van Haesendonck C, Bruynseraede Y, Kwarciak J and Van der Biest O 1990 *J. Less Common Metals* 164-165 663
- [205] Tanaka K, Nozue A and Kamiya K 1990 *J. Mater. Sci.* 25 3551
- [206] Masuda Y, Ogawa R, Kawate Y, Tateishi T and Hara N 1992 *J. Mater. Res.* 7 292
- [207] Mahesh R, Nagarajan R and Rao C N R 1992 *J. Solid State Chem.* 96 2
- [208] Ham W K, Holland G F and Stacy A M 1988 *J. Am. Chem. Soc.* 110 5214
- [209] Subramanian M A, Gopalakrishnan J, Torardi C C, Askew T R, Flippen R B, Sleight A W, Liu J J and Poon J J 1988 *Science* 240 495
- [210] Rudolf P and Schöllhorn R 1992 *JCS Chem. Commun.* 1158
- [211] Coppa N, Nichols D H, Schwegler J W, Crow J E, Myer G H and Salomon R E 1989 *J. Mater. Res.* 4 1307; Coppa N, Kebede A, Schwegler J W, Perez I, Salomon R E, Myer G H and Crow J E 1990 *J. Mater. Res.* 5 2755
- [212] Merzhanov A G and Borovinskaya I P 1972 *Dokl. Acad. Nauk.* 204 366
- [213] Mahesh R, Vikram A Pavate, Om Prakash and Rao C N R 1992 *Supercond. Sci. Technol.* 5 174
- [214] Varma H, Warrier K G and Damodaran A D 1990 *J. Am. Ceram. Soc.* 73 3103
- [215] Pederson L R, Maupin G D, Weber W J, McReady D J and Stephens R W 1991 *Mater. Lett.* 10 437
- [216] Sundar Manoharan S, Prasad V, Subramanyam S V and Patil K C 1992 *Physica C* 190 225
- [217] Lepart J P and Varma A 1991 *Physica C* 184 220
- [218] Kourtakis K, Robbins M and Gallagher P K 1989 *J. Solid State Chem.* 82 290
- [219] Kourtakis K, Robbins M, Gallagher P K and Tiefel T 1989 *J. Mater. Res.* 4 1289
- [220] Tomizawa T, Matsunaga H, Fujishiro M and Kakegawa H 1990 *J. Solid State Chem.* 89 212
- [221] Tripathi R B and Johnson D W Jr 1991 *J. Am. Ceram. Soc.* 74 247
- [222] Horn J, Borner H, Semmelhack H C, Lippold B, Hermann J, Wurlitz M, Krotzsch M, Boehne U, Schlenkrich F and Frenzel Ch 1991 *Solid State Commun.* 79 483
- [223] Song K H, Liu H K, Dou S and Sorrell C C 1990 *J. Am. Ceram. Soc.* 73 1771
- [224] Matsuzaki K, Inoue A, Kimura H, Aoki K and Masumoto T 1987 *Japan. J. Appl. Phys.* 26 L1310
- [225] Kogure T, Kontra R, Yurek G J and Vander Sande J B 1988 *Physica C* 156 45
- [226] Grenier J C, Wattiaux A, Lagueyte N, Park J C, Marquestaut E, Etourneau J and Pouchard M 1991 *Physica C* 173 139

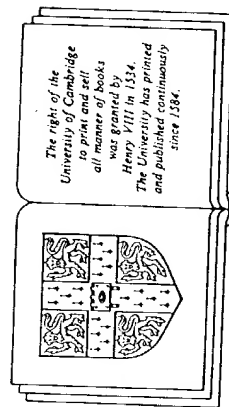
# ATTACHMENT D

C. N. R. RAO, FRS  
J. GOPALAKRISHNAN

*Solid State and Structural Chemistry Unit, Indian Institute of Science,  
Bangalore, India*

# New directions in solid state chemistry

Structure, synthesis, properties, reactivity  
and materials design



CAMBRIDGE UNIVERSITY PRESS  
*Cambridge*

*London New York New Rochelle  
Melbourne Sydney*

SCICOL  
QD  
478  
R36  
1986

## Contents

Published by the Press Syndicate of the University of Cambridge  
The Pitt Building, Trumpington Street, Cambridge CB2 1XP  
32 East 57th Street, New York, NY 10022, USA  
10 Stanford Road, Oakleigh, Melbourne 3166, Australia

© Cambridge University Press 1986

First published 1986

Printed in Great Britain at the University Press, Cambridge

*British Library cataloguing in publication data*

Rao, C. N. R.

New directions in solid state chemistry: structure,  
synthesis, properties reactivity and materials design.-  
(Cambridge solid state science series)

I. Solid state chemistry

I. Title II. Gopalakrishnan, J.

541'.0421 QD478

*Library of Congress cataloguing in publication data*

Rao, C. N. R. (Chintamani Nagesa Ramachandra), 1934-

New directions in solid state chemistry.

(Cambridge solid state science series)

Includes bibliographical references.

I. Solid state chemistry. I. Gopalakrishnan,

J. (Jagannatha), 1939- II. Title. III. Series.

QD478.R36 1986 541'.0421 85-22329

ISBN 0 521 301920

Preface	ix
1 Structure of solids: old and new facets	1
1.1 Introduction	1
1.2 Description of crystals	2
1.3 Bonding in crystals	4
1.4 Inorganic structures	13
1.5 Silicates and aluminosilicates	34
1.6 Nonbonded interactions in ionic crystals	39
1.7 New ways of looking at the structures of inorganic solids	42
1.8 Polytypism	50
1.9 Organic crystal structures	53
1.10 Inclusion compounds and clathrates	56
1.11 Noncrystalline or amorphous solids	60
1.12 Quasicrystals	65
1.13 Models and graphics	65
1.14 Solitons	66
2 New and improved methods of characterization	67
2.1 Introduction	67
2.2 Structural characterization	68
2.2.1 X-ray diffraction	70
2.2.2 Electron diffraction	71
2.2.3 Neutron diffraction and related techniques	73
2.2.4 Electron microscopy	75
2.2.5 X-ray absorption spectroscopy (EXAFS and XANES)	84
2.2.6 Nuclear magnetic resonance spectroscopy (MASNMR)	95
2.2.7 Electron spectroscopies	99
2.2.8 Other spectroscopic techniques	105
2.2.9 Concluding remarks	106
2.3 Characterization of composition and purity	107
3 Preparative strategies	112
3.1 Introduction	112
3.2 Preparation of crystalline materials	116
3.2.1 Ceramic methods	116

TM

bulk metals. Metal particulates (similar to those on the surfaces of supported metal catalysts (Chapter 8)) constitute a type of metal aggregate somewhere between high nuclearity metal clusters and bulk metals.

There are families of metal cluster compounds (Fig. 6.37) containing metal clusters surrounded by ligands (Lewis & Green, 1982). In small cluster compounds, the electrons are paired, but in large clusters there will be closely spaced electronic levels, as in metal particles. In such clusters, quantum size effects would be expected. Benfield *et al.* (1982) have found intrinsic paramagnetism in  $\text{H}_2\text{Os}_{10}(\text{CO})_{24}$  below 70 K as expected of an osmium particle of approximate diameter of 10 Å; the excess paramagnetism increases with cluster size in osmium compounds (Johnson *et al.*, 1985).

Metal cluster compounds simulate surface species produced by the interaction of molecules with metal surfaces (Muetterties *et al.*, 1979) and this is of value in understanding heterogeneous catalysis. The development of selective catalysts for the  $\text{C}_1$  chemical industry employing CO (and possibly  $\text{CO}_2$ ) as the raw material has resulted in major efforts in metal cluster research. Criteria have been developed to distinguish between cluster catalysis and mononuclear catalysis. Typical of the catalysts investigated hitherto are  $[\text{Ir}_4(\text{CO})_{12-x}(\text{PPh}_3)_x]$  where  $\text{Ph} = \text{phenyl}$  and  $x = 1, 2$  or 3.

## 6.7 Mixed-valence compounds

Chemical compounds consisting of an element (usually a metal) in two different formal oxidation states are said to exhibit mixed valency. Mixed-valence chemistry is as old as chemistry itself, some of the well known mixed-valence compounds being Prussian blue ( $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 14\text{H}_2\text{O}$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), and heteropoly tungsten and molybdenum blues. Mixed-valence chemistry, however, encompasses a large variety of solids with fascinating properties (Table 6.6) formed by nearly a third of the elements in the periodic table, and there has been a recent upsurge of interest in the subject (Day, 1981). Since variable valency is a prerequisite for mixed valency, it is quite common among the compounds of transition metals, Ce, Eu and Tb, as well as some of the post-transition elements with stable  $ns^2$  and  $ns^0$  electronic configurations such as Ga, Sn, Sb, Tl, Pb and Bi. Most mixed-valency compounds contain electronegative counterpart anions such as halides, oxide, sulphide or molecular ligands containing electronegative atoms. In order for a solid to be called a mixed-valence compound, we should be able to assign definite oxidation states that differ by integral numbers (one or at the most two units) to the element showing mixed valency.

$\text{Fe}_3\text{O}_4$  consisting of iron in the  $2^+$  and  $3^+$  oxidation states, is a mixed-valence compound, whereas the alloy  $\text{Nb}_3\text{Ge}$ , where we cannot specify the oxidation states of the constituents, is not. We should also make a distinction between the mixed-valence compounds of the  $\text{Fe}_3\text{O}_4$  type and valence-fluctuating systems such as Ce and SmS, where a fluctuation in the electron configuration between  $4f^n$  and  $4f^{n-1}d^1$  occurs (Falicov *et al.*, 1981). (see Section 2.2.7). Electronic properties associated with  $f$ -electrons receiving much attention recently are those arising from heavy fermion behaviour (e.g.  $\text{CeCu}_2\text{Si}_2$ ,  $\text{UPt}_3$ ) wherein the carriers exhibit large effective masses (Stewart, 1984).

In certain mixed-valence compounds, the presence of more than one oxidation state can be recognized from the formula, as for example  $\text{Pb}_3\text{O}_4$  and  $\text{V}_n\text{O}_{2n-1}$ , while in some others the formula indicates an apparently integral oxidation state although the oxidation state is rather unusual for the element in question. Typical examples of the latter category are  $\text{Sb}_2\text{O}_4$ ,  $\text{BaBiO}_3$  and  $\text{Pt}(\text{NH}_3)_2\text{Cl}_3$ ; experimental evidence shows that we are not dealing with Sb(IV), Bi(IV) and Pt(III) states in these compounds but with Sb(III, V), Bi(III, V) and Pt(II, IV), and these solids should indeed be formulated as  $\text{Sb}^{3+}\text{Sb}^{5+}\text{O}_4$ ,  $\text{BaBi}_{0.5}^{3+}\text{Bi}_{0.5}^{5+}\text{O}_3$  and  $[\text{Pt}(\text{NH}_3)_4]^{2+}[\text{PtCl}_6]^{2-}$ . In all such systems, X-ray photoelectron

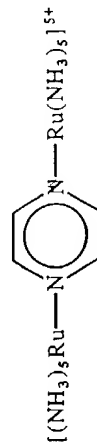
Table 6.6 Typical mixed-valence solids

Compound	Classification in the Robin-Day scheme	Importance
$\text{Pb}_3\text{O}_4$	Class I	Red lead
$\text{Sb}_2\text{O}_4$	Class I	Mineral cervantite
$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 14\text{H}_2\text{O}$	Class II	Dye and pigment (Prussian blue)
$\text{V}_n\text{O}_{2n-1}$	Class II	Semiconductor-metal transitions
$\text{Li}_x\text{Ni}_{1-x}\text{O}$	Class II	Hopping semiconductor
$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$	Class II	Ferromagnetism
$\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$	Class III	Superconductivity
$\text{LiTi}_2\text{O}_4$	Class III	Superconductivity
$\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.30} \cdot 3\text{H}_2\text{O}$	Class III	Molecular metal; Peierls instability
$\text{Na}_x\text{WO}_3$	Class III	Bronze lustre and metallic at high $x$
$\text{M}_x\text{Mo}_6\text{S}_8$	Class III	Superconductivity
$\text{Fe}_4\text{S}_4$ Ferredoxins	Class III	Electron transfer (enzymes)

spectroscopy can readily identify the presence of mixed valency (Rao *et al.*, 1979).

Robin & Day (1967) have proposed a classification of mixed-valence compounds based on the valence delocalization coefficient,  $\alpha$ , the magnitude of which depends on the energy difference between the two states  $M_A^{n+}M_B^{(n+1)+}$  and  $M_A^{(n+1)+}M_B^{n+}$ , where A and B are two different sites. When  $\Delta E$  is large as in  $Pb_3O_4$ ,  $\alpha$  is small; such compounds belong to class I. If the two sites are similar but crystallographically distinguishable, the compounds are considered to belong to class II. In class III,  $\alpha$  becomes large and the two sites occupied by the mixed-valent cations are identical. Properties associated with the different classes would be different (Table 6.6). For example, in class I compounds, electron hopping between the sites is not favoured since  $\Delta E$  is large. In class III compounds, on the other hand, the electrons would be delocalized. The ligands which bridge the cations play a role in determining the intervalence transfer; the greater the metal-ligand overlap, the higher the probability of electron transfer (Mayoh & Day, 1972). In order to describe the electron transfer in mixed-valence compounds properly, one would have to consider the coupling between the electronic and vibrational motions. Experimentally, the frequency of optical intervalence transition gives an estimate of the energy required for thermally activated electron transfer. The intensity of the optical intervalence transition gives information on  $\alpha$ . One of the most characteristic features of mixed-valent class II compounds is the structureless broad intervalence absorption band in the visible and infrared. A vibrational coupling model has been developed to calculate the absorption profiles (Piepho *et al.*, 1978); a good example of analysis of such absorption profiles is the recent study of  $(CH_3NH_3)_2Sb_xSn_{1-x}Cl_6$  by Prassides & Day (1984). When the electrons are not completely delocalized and they hop from site to site in marginal semiconductors, the strength of interaction between the electrons and the lattice (polarons) becomes an important factor.

Mixed valency occurs in minerals (e.g.  $Fe_3O_4$ ), metal-chain compounds, dimers and oligomers and metal complexes, and even in organic and biological systems (Brown, 1980; Day, 1981). Among the dimeric and oligomeric metal complexes exhibiting mixed valency, the pyrazine-bridged Ru (II, III) ammine complex,



synthesized by Creutz & Taube (1973), has received much attention. The important question with regard to this family of complexes is whether they belong to class II or III. With identical ligands around each metal ion, the first impression is to consider the *Creutz-Taube complex* as belonging to class III. Optical absorption shows an intense band in the visible (550 nm), which is characteristic of Ru(II). It certainly supports the idea that a distinct Ru(II) can be identified on the time scale of optical transition ( $10^{-14}$  s). However, the intervalence band centred at  $\sim 1550$  nm is insensitive to solvent effects and a bit too narrow to be called a class II behaviour. XPS shows doublets in the core-level Ru(3d) and (3p) spectra, indicating that the individual oxidation states can be distinguished on this time scale ( $10^{-16}$  s) as well. Hush (1975) has argued that the creation of core-hole by photoionization would relax the system into a localized state even if it were originally delocalized; core-shell photoelectron spectroscopy therefore does not appear to provide the means to determine the extent of localization or delocalization in the valence shell. Infrared spectroscopy has shown that the  $NH_3$  rocking mode ( $800\text{ cm}^{-1}$ ),  $Ru-NH_3$  stretching mode ( $449\text{ cm}^{-1}$ ) and  $Ru$ -pyrazine stretching mode ( $316\text{ cm}^{-1}$ ) of the Creutz-Taube complex all occur at values intermediate between those of the corresponding Ru(II) and Ru(III) complexes. This has been taken as evidence that the valence electron is delocalized in the time scale of infrared spectroscopy ( $10^{-12}$ – $10^{-13}$  s). Results of the various measurements on this complex are somewhat conflicting because of the different time scales; it appears that the electron-transfer rate is somewhere between  $10^5$ – $10^{12}\text{ s}^{-1}$ . Mixed valency in compounds like  $La_{1-x}Sr_xCoO_3$  (Rao *et al.*, 1975, 1977) is determined by rate of electron transfer and so by composition; that in  $MoFe_2O_4$  and other solids resulting from fast electron transfer is discussed (Ramdani *et al.*, 1985).

In the metal-chain compounds, we can distinguish two types of mixed valent systems, one where the chain is entirely composed of metal atoms (class III) and the other in which the metal and the bridging ligand alternate (class II). Wolfram's red salt,  $[Pt(C_2H_5NH_2)_4][Pt(C_2H_5NH_2)_4Cl_2] \cdot 4H_2O$  is an example of the former, consisting of Pt(II) and Pt(IV) ions bridged by chloride ions. In KCP type of mixed-valent compounds, mixed valency is achieved by partly oxidizing the Pt ions to an average oxidation state  $(2+x)$  with  $x \approx 0.3$ . Partial oxidation is accomplished by removing some of the cations as in  $K_{1.75}Pt(CN)_4 \cdot 1.5H_2O$  or by introducing extra anions  $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$ . Even the Hg chain compound  $Hg_{3-x}AsF_6$  (see Section 4.9) is mixed-valent.

$\text{Fe}_3\text{O}_4$  has the inverse spinel structure, with all the  $\text{Fe}^{2+}$  ions and half of the  $\text{Fe}^{3+}$  ions located in octahedral sites (B sites) in the oxygen network and the remaining half of the  $\text{Fe}^{3+}$  ions located on tetrahedral sites (A sites). It undergoes a ferrimagnetic-paramagnetic transition around 850 K and another transition around  $T_V = 123$  K (Verwey transition). The material is a semiconductor both above and below the Verwey transition. Some changes in properties have also been observed near 200 K and 12 K, but these are not very significant. The properties of  $\text{Fe}_3\text{O}_4$  in the region of the Verwey transition and above have been a subject of great interest, and an entire issue of the *Philosophical Magazine* (B42, No. 10, 1980) was devoted to the transition.

Detailed structural investigations employing neutron diffraction and other techniques suggest that charge ordering of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions (and therefore the long-range order) is established below  $T_V$ . Cation strings,  $a$  and  $b$ , run along the  $[110]$  and  $[1\bar{1}0]$  directions respectively (on alternate (001) planes). While three  $\text{Fe}^{2+}$  ions in succession are followed by a  $\text{Fe}^{3+}$  ion along one  $a$  chain, on an adjacent  $a$  chain three  $\text{Fe}^{3+}$  ions are followed by one  $\text{Fe}^{2+}$ . In the  $b$  chain, cation ordering occurs with a pair of  $\text{Fe}^{3+}$  ions followed by a pair of  $\text{Fe}^{2+}$  ions in alternation. Successive  $-b-a-b-$  planes are stacked, perpendicular to the  $c$  axis, in such a way that proximate cations in three successive planes are in groups, forming hexagonal rings of alternate  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions. All the cations along  $b$  strings are members of rings and only a quarter of the  $a$ -string cations are involved in ring formation. The synchronous displacement of three electrons to their nearest-neighbour position inside any ring produces an interchange of  $\text{Fe}^{2+}$  with  $\text{Fe}^{3+}$ . A significant fraction of hexagonal rings always exists in the 'inverted' charge configuration, thereby randomizing charge along the  $b$  strings, but leaving three-quarters of the  $a$ -chain constituents in an ordered arrangement below  $T_V$ . This rationalizes earlier experimental findings that it is the  $a$ -plane cations which order at low temperatures.

The existence of superstructure lines just above  $T_V$  in critical neutron scattering and the detailed investigation of elastic and inelastic neutron scattering show the existence of a soft mode with wave vector  $k = (00\frac{1}{2})$  that 'condenses' at  $k = (00\frac{1}{2})$ . Proceeding from one  $\text{Fe}^{2+}$  (or from one  $\text{Fe}^{3+}$ ) ion in the  $a$  plane at  $z = \frac{1}{8}$  to the corresponding position in the  $a$  plane at  $z = \frac{7}{8}$ , one arrives at the complementary charge (namely,  $\text{Fe}^{3+}$  or  $\text{Fe}^{2+}$ ) respectively. One has to advance by twice the unit lattice distance along  $c$  to duplicate the same ionic configuration at  $z = \frac{1}{8}$  that prevails at  $z = \frac{7}{8}$ . Formally, this corresponds to the existence of a charge-density wave (with wave length  $\lambda = 2c$ ) which couples strongly to the corresponding phonon mode with the same wave vector. At the transition, the ordering of the charges (leading to the establishment of the CDW)

occurs simultaneously with a net atomic displacement that lowers the symmetry.

Although the structural characterization of  $\text{Fe}_3\text{O}_4$  near the Verwey transition is fairly satisfactory, many finer details are not yet understood, (Honig, 1982, 1986), including the actual structure of the low-temperature phase (rhombohedral, orthorhombic, monoclinic or triclinic). Electrical properties around  $T_V$  are also not fully characterized. There is uncertainty regarding the nature of variation of conductivity with temperature. It is not clear whether the itinerant character of charge carriers assumed by some workers is valid. Most of the data on transport properties seem to suggest a small polaron model. What is rather puzzling is that the resistivity decreases by two orders of magnitude at  $T_V$ , accompanied by the loss of long-range order. Recent studies have shown that the Verwey transition and the associated changes in conductivity and heat capacity are very sensitive to oxygen stoichiometry (Honig, 1986).

There are several interesting families of inorganic mixed-valence compounds that we have not discussed here (see Yvon, 1979; McCauley, 1982). For example, there are metal-cluster compounds such as the Chevrel phases,  $\text{M}_x\text{Mo}_6\text{X}_8$  ( $X = \text{S}$  or  $\text{Se}$ ) and condensed metal-cluster chain compounds such as  $\text{TiMo}_3\text{Se}_3$ ,  $\text{Ti}_3\text{Te}_4$ ,  $\text{NaMo}_4\text{O}_6$  and  $\text{M}_x\text{Pt}_3\text{O}_4$ . TTF halides and TTF-TCNQ complexes (Section 1.9) constitute molecular mixed-valent systems in which the mixed valency is associated with an entire molecule; the charge on TTF in such compounds is non-integral. The structure of  $\text{TTF}-\text{Br}_{0.79}$  and such solids consists of stacks of TTF molecules parallel to the  $c$ -axis. The  $\text{Br}^-$  ions are also arranged in columns parallel to the  $c$ -axis. However, the repeat distances of the cation ( $3.57 \text{ \AA}$ ) and anion ( $4.54 \text{ \AA}$ ) columns are different (Fig. 6.38). The structure is incommensurate along the  $c$ -axis because the lattice periodicities of the two subunits are not simple multiples (or fractions) of one another. It is important to note that the periodicity of the TTF sublattice is independent of stoichiometry, whereas that of the bromide sublattice is stoichiometry dependent. Hence the charge transfer in the salt can be expressed as  $f = 3.57/c(\text{Br})$ . Nonstoichiometric compositions in the TTF-halide systems seem to be stabilized because of electrostatic (Madelung) factors. Calculations show that the Madelung energy is maximum around a halogen content of 0.7 to 0.8. Beyond this composition, repulsion between like charges along the stacking axis begins to dominate, decreasing the net binding energy. Optical absorption shows a new peak around 0.7 eV in  $\text{TTF}-\text{Br}_{0.79}$ . The peak, which is not present in the spectra of stoichiometric salts, has been assigned to a mixed-valence intrastack charge-transfer transition between a neutral TTF and adjacent  $\text{TTF}^+$ .

The structure of HMTTF-TCNQ, a typical TTF-TCNQ-type complex, is shown in Fig. 6.39. The segregated stacking in this structure is a characteristic feature of the highly conducting organic charge-transfer system of the TTF-TCNQ family. In HMTTF-TCNQ (HMTTF-hexamethylenetetrafulvalene), the separation between donor molecules is 3.57 Å while that between TCNQ molecules is 3.23 Å along the stacks. To make the anion and cation sublattices com-

Figure 6.38. Crystal structure of TTF-Br<sub>0.79</sub>. Projections (a) down the *a*-axis and (b) down the *b*-axis. (After Torrance & Silverman, 1977.)

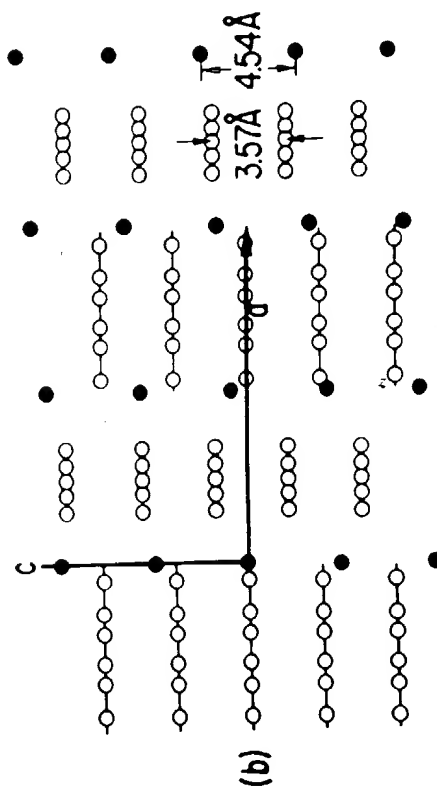
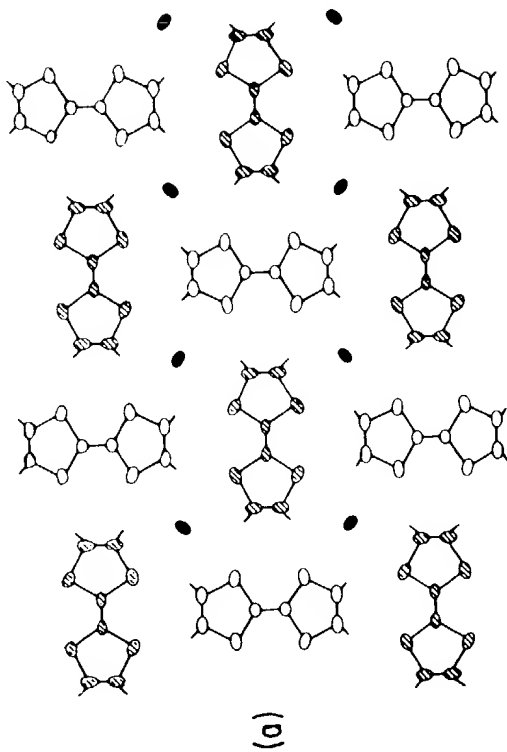


Figure 6.39. Crystal structure of HMTTF-TCNQ. (a) Projection on the plane perpendicular to the stacking axis and (b) projection on a plane containing the stacking axis. (After Greene *et al.*, 1976.)

mensurate with each other, the molecules are stacked in a staggered configuration such that the normals to the molecular planes are not parallel to the stacking axis but make an angle with it. The angles are different for the donor and acceptor stacks; in the HMTTF-TCNQ structure, the values are respectively 23.8° and 34.2°.

What makes the TTF-TCNQ family distinct from the other salts of TCNQ with cations, such as alkali metals and tetramethylammonium, is



that the charge transfer,  $f$ , in the TTF-TCNQ family is incomplete ( $f < 1$ ). TTF-TCNQ members are also different from the TTF-halides; in the TTF-halides, where the charge on each halide atom is unity, partial charge transfer (mixed valency) is realized by the formation of non-stoichiometric materials, while in the TTF-TCNQ family, the composition is stoichiometric (1:1), but mixed valence arises because of partial electron-transfer.

Evidence for incomplete electron transfer (mixed valency) has come from a number of physical studies. Optical absorption studies show a low energy peak at 0.3 eV, which is not present in insulating salts such as  $K^+(TCNQ)^-$ . Moreover, the absorption is polarized parallel to the stack axis. The absorption is therefore clearly due to mixed-valence intrastack electronic transition. TTF-TCNQ undergoes a transition from conducting to insulating state at 59 K. This transition is characterized by a subtle periodic modulation of the lattice due to a coupling of the conduction electrons with the lattice (CDW). This shows up in the form of satellite reflections surrounding the Bragg peaks in the diffraction experiment. Because the structure is sinusoidally modulated, the Bragg peaks caused by the average structure remain essentially unchanged. Since the satellite peaks are the result of interaction between conduction electrons and the lattice, their positions are determined by the extent of charge transfer  $f$ ; a value of  $f = 0.59$  has been obtained for TTF-TCNQ from the diffraction satellites. A comparison of charge transfer in a variety of TCNQ salts with the reduction potential of cations shows that only those cations with a reduction potential  $E_r = 0.0$  to 0.5 V vs. SCE lead to mixed-valence or incomplete transfer (Torrance, 1979). When the potential is too high (perylene, pyrene, anthracene etc.), there is no charge transfer and when it is too low, the transfer is complete.

The effect of  $f$  on the conductivity of TCNQ salts can be visualized as follows: for electrical conduction to occur, electrons must move from one TCNQ to another. When the charge transfer is complete, the process can be represented as



which involves creation of a dianion. Understandably the energy involved would be prohibitive and hence TCNQ salts with  $f = 1$  are insulators. In the mixed-valence salts, the electrons can move easily along the stack by the process,  $TCNQ^- + TCNQ^{\circ} \longrightarrow TCNQ^{\circ} + TCNQ^-$ , which does not require creation of dianions. This localized picture is, however, only qualitative. A more accurate description would involve the band model. The relation between mixed-valence and

electrical properties is seen in HMTTF-TCNQ and HMTTF-TCNQF<sub>4</sub>. Both are isostructural but HMTTF-TCNQ is metallic, while the tetrafluoro-substituted TCNQ salt is semiconducting; the conductivity of the latter is about seven orders of magnitude less than the former. This difference arises because TCNQF<sub>4</sub> is a much stronger acceptor than TCNQ and hence the charge transfer is complete in HMTTF-TCNQF<sub>4</sub>.

## 6.8 Low-dimensional solids

Chemists are by and large preoccupied with three-dimensional structures and most of solid state chemistry deals with three-dimensional solids. However, there has been increasing interest in lower-dimensional solids which show spectacular anisotropy in their properties. One is familiar with graphite that is metallic in two dimensions and a semiconductor in the third dimension; the striking directional differences in the properties of mica(sheet) and asbestos (fibre) are common experience. The platinum chain compound KCP (referred to earlier reflects visible light and conducts electricity like a metal only in the chain direction. If one looks at a crystal of KCP with a polaroid oriented so that the electric vector of the light is parallel to the chain axis, it is highly reflecting and copper-coloured; if the polaroid is turned through a right angle, it is pale yellow and transparent like any other ionic crystal. The situation is similar with Wolfram's red salt. Most of the synthetic metals or molecular metals are low-dimensional solids; many of the exotic materials being tried for superconductivity are also low-dimensional (Keller 1975, 1977; Miller & Epstein, 1978; Hatfield, 1978; Alcaer, 1980; Miller, 1982).

It is convenient to classify low-dimensional solids into two categories, chain (essentially one-dimensional) and layer (essentially two-dimensional). Examples of the chain compounds are KCP and other Pt-chain compounds, polymeric (SN)<sub>x</sub>, polyacetylene, Hg<sub>3-x</sub>AsF<sub>6</sub> with Hg chains, [(CH<sub>3</sub>)<sub>4</sub>N]MnCl<sub>3</sub>, KCuF<sub>3</sub> and RbFeCl<sub>3</sub>. Examples of layer compounds are graphite-related systems, Ta and Nb chalcogenides, K<sub>2</sub>NiF<sub>4</sub>, (RNH<sub>3</sub>)<sub>2</sub>MCl<sub>4</sub> and CoCl<sub>2</sub> (R = CH<sub>3</sub> etc., M = Cr, Mn etc.). We shall briefly examine the magnetic, electrical and optical properties as well as phase transitions of typical members of this extraordinary class of materials. (Day, 1983; Subramanyam & Naik, 1985.) also see Phil. Trans. Roy. Soc. London 1985, A314.

In understanding the magnetic behaviour of solids it is necessary to take into account not only the dimensionality of the lattice (1 to 3), but also the dimensionality of the spin or of the order parameter (1 to 3), which give rise to nine possible types of magnetic systems. In addition,



**UNITED STATES DEPARTMENT OF COMMERCE**  
**Patent and Trademark Office**

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.
-----------------	-------------	----------------------	---------------------

00/363,801

02/05/94

REMARKS

MT  
ATTORNEY (US3)

EXAMINER

DANIEL F. RUPPEL  
IBM CORPORATION  
INTELLECTUAL PROPERTY LAW DEPARTMENT  
P.O. BOX 218  
YORKTOWN HEIGHTS NY 10590

ART UNIT

PAPER NUMBER

DATE MAILED: 5/17/94

Please find below and/or attached an Office communication concerning this application or proceeding.

Commissioner of Patents and Trademarks

IBM  
YORKTOWN  
2000 MAY 22 AM 10:08  
INTELLECTUAL PROPERTY  
LAW DEPT.



UNITED STATES DEPARTMENT OF COMMERCE  
Patent and Trademark Office  
ASSISTANT SECRETARY AND COMMISSIONER OF  
PATENTS AND TRADEMARKS  
Washington, D.C. 20231

BEFORE THE BOARD OF PATENT APPEALS  
AND INTERFERENCES

Paper No. 90

Application Number: 08/303,561  
Filing Date: September 09, 1994  
Appellant(s): Johannes G. Bednorz et al.

MAILED

MAY 17 2000

GROUP 1700

Daniel P. Morris  
For Appellant

EXAMINER'S ANSWER

MAILED

MAY 09 2000

GROUP 1700

This is in response to appellant's brief on appeal  
filed 1/18/2000 (Substitute Brief).

**(1) Real Party in Interest**

A statement identifying the real party in interest is  
contained in the brief.

IBM  
YORKTOWN  
2000 MAY 22 AM 10:08  
INTELLECTUAL PROPERTY  
LAW DEPT.

Art Unit: 1751

**(2) *Related Appeals and Interferences***

A statement identifying the related appeals and interferences which will directly affect or be directly affected by or have a bearing on the decision in the pending appeal is contained in the brief.

**(3) *Status of Claims***

The statement of the status of the claims contained in the brief is incorrect. A correct statement of the status of the claims is as follows:

Claims 24-26, 86-90, 96-177 are pending.

Claim 136 was allowed at the time of Final Rejection. Claims 114-116, 119-121, 124-126, 132, 133, 137, 138, 143, 144, 146, 148, 152-157, 160-163, 167, 168, 171, 172 and 173 have been subsequently allowed. Reasons for the withdrawal of the previous rejections as they pertain to these claims will appear in section (6) Issues of Rejection of this Examiner's Answer.

Claims 24-26, 88-90, 96-102, 109-113, 129-131, 134, 135, 139-142, 145, 149-151, 158, 159, 164-166, 169-170 and 174-177 remain rejected under 35 U.S.C. 112, first paragraph.

Claims 86, 87, 96-108, 112, 113, 117, 118, 122, 123, 127, 128 and 147 remain rejected under 35 U.S.C. 112, second paragraph.

Art Unit: 1751

**(4) Status of Amendments After Final**

The appellant's statement of the status of amendments after final rejection contained in the brief is correct.

Note that an additional complete record of these after-final submissions also appears in Paper #88 (Notification of Non-Compliance mailed 9/13/99). Note also that in appellant's original Brief filed 7/1/99, at page 4, reference is made to an after-final submission filed 12/14/98. In Paper #88 (Notification of Non-Compliance mailed 9/13/99) appellant was requested to clarify the status of the 12/14/98 submission. In the Substituted Brief filed 1/18/00 no reference is made to the 12/14/98 submission. Accordingly, the Examiner believes the record to be complete with respect to after-final submissions as delineated by appellant in the Substitute Brief filed 1/18/00.

**(5) Summary of Invention**

The summary of invention contained in the brief is correct.

**(6) Issues**

The appellant's statement of the issues in the brief is substantially correct. The changes are as follows:

Are claims 24-26, 88-90, 96-102, 109-113, 129-131, 134, 135, 139-142, 145, 149-151, 158, 159, 164-166, 169-170 and 174-177 not enabled under 35 U.S.C. 112, first paragraph.

Art Unit: 1751

Are claims 86, 87, 96-108, 112, 113, 117, 118, 122, 123, 127, 128 and 147 indefinite under 35 U.S.C. 112, second paragraph.

The prior art rejection over Asahi Shinbum, International Satellite Edition (London), November 28, 1986 (hereinafter, "the Asahi Shinbum article") is withdrawn in view of applicant's remarks.

Upon careful consideration, the examiner agrees with applicant's position appearing at pages 39-44 of the supplemental response filed 8/5/99. Specifically, applicant has sufficiently demonstrated conception, diligence and reduction to practice of the instant invention before the publication date of the Asahi Shinbum article. Applicants have shown that conception of their invention was in the United States at their direction prior to the publication date of the reference. As explicitly stated in *Wilson v. Sherts*, 81 F2d 755, 28 USPQ 379 (CCPA 1936), "In the case of conception and reduction to practice, it is well settled that the conception must take place in the United States, or in lieu thereof, it must have been brought to this country or must have been communicated to someone in this country.". Such has been shown by applicants.

Art Unit: 1751

Accordingly, the issue of claims 24-26, 86-90, 96-135 and 137-177 being supported by the priority document is believed moot in view of the withdrawal of the prior art rejections.

**(7) Grouping of Claims**

The appellant's statement in the brief that certain claims do not stand or fall together is not agreed with because appellant merely states "Each claim is appealed individually" but fails to present any detailed reasoning in support of such a statement.

**(8) Claims Appealed**

The copy of the appealed claims contained in the Appendix to the brief is correct.

**(9) Prior Art of Record**

No prior art is relied upon by the examiner in the rejection of the claims under appeal.

**(10) Grounds of Rejection**

The following ground(s) of rejection are applicable to the appealed claims:

The specification is objected to under 35 U.S.C. § 112, first paragraph, as failing to provide an enabling disclosure commensurate with the scope of the claims.

Art Unit: 1751

The present specification is deemed to be enabled only for compositions comprising a transition metal oxide containing at least a) an alkaline earth element and b) a rare-earth element or Group IIIB element. The art of high temperature (above 30°K) superconductors is an extremely unpredictable one. Small changes in composition can result in dramatic changes in or loss of superconducting properties. The amount and type of examples necessary to support broad claims increases as the predictability of the art decreases.<sup>1</sup> Claims broad enough to cover a large number of compositions that do not exhibit the desired properties fail to satisfy the requirements of 35 U.S.C. 112.<sup>2</sup> Merely reciting a desired result does not overcome this failure.<sup>3</sup> In particular, the question arises: Will any layered perovskite material exhibit superconductivity?

It should be noted that at the time the invention was made, the theoretical mechanism of superconductivity in these materials was not well understood. That mechanism still is not understood. Accordingly, there appears to be little factual or theoretical

---

<sup>1</sup>See In re Fisher, 166 USPQ 18, 24; and In re Angstadt and Griffen, 190 USPQ 214, 218. See also, In re Colianni, 195 USPQ 150, 153, 154 (CCPA 1977) (J. Rich).

<sup>2</sup>See In re Cook, 169 USPQ 298, 302; and Cosden Oil v. American Hoechst, 214 USPQ 244, 262.

<sup>3</sup>See In re Corkill, 226 USPQ 105, 1009.



Art Unit: 1751

basis for extending the scope of the claims much beyond the proportions and materials actually demonstrated to exhibit high temperature superconductivity. A "patent is not a hunting license. It is not a reward for the search, but a reward for its successful conclusion".<sup>4</sup>

Note that the above 112, first paragraph, rejection has been modified in scope from the Final Office Action. Upon careful consideration of the evidence as a whole, including the specification teachings and examples, and applicant's affidavits and remarks, the examiner has determined that the instant specification is enabled for compositions comprising a transition metal oxide containing an alkaline earth element and a rare-earth or Group IIIB element (as opposed to only compositions comprising  $\text{Ba}_x\text{La}_{3-x}\text{Cu}_3\text{O}_y$  as stated in the Final Office action). Applicant has provided guidance throughout the instant specification that various transition metal oxides (such as copper oxide) containing an alkaline earth element and a rare-earth or Group IIIB element result in superconductive compounds which may in turn be utilized in the instantly claimed methods.

Claims 24-26, 88-90, 96-102, 109-113, 129-131, 134, 135, 139-142, 145, 149-151, 158, 159, 164-166, 169-170 and 174-

---

<sup>4</sup>See Brenner v. Manson, 383 US 519, 148 USPQ 689.

Art Unit: 1751

177 are rejected under 35 U.S.C. § 112, first paragraph, for the reasons set forth in the objection to the specification.

Claims 86, 87, 96-108, 112, 113, 117, 118, 122, 123, 127, 128 and 147 are rejected under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

With respect to claims 86, 87, 96-108, 112, 113, 117, 118, 122, 123, 127, 128 and 147, the terms "layer-type", "perovskite-like", "rare-earth-like" are vague and confusing.

The question arises: What is meant by these terms?

The terms "layer-type" and "perovskite-like" are unclear because the "type" or "like" terms are deemed to be indefinite. Terms such as "like", "similar", and "type" are indefinite.<sup>5</sup> It is suggested that "layer-type perovskite-like crystal structure" be changed -- a substantially layered perovskite crystal structure --.

Note that claims 112, 113, 117, 127 and 128 were not listed in the heading of this rejection in paper #66 (Final Rejection mailed 6/25/98). However, each claim clearly contains the exact

---

<sup>5</sup>See Ex parte Remark, 15 USPQ 2d 1498, 1500 (BPAI 1990); Ex parte Kristensen, 10 USPQ 2d 1701, 1703 (BPAI 1989); Ex parte Attig, 7 USPQ 2d 1092, 1093 (BPAI 1988); and Ex parte Copenhaver, 109 USPQ 118 (POBA 1955).

Art Unit: 1751

language referred to in the body of the rejection, and claims 112, 113, 117 are specifically referenced at page 13 of the Final rejection in the examiner's discussion of the 112, second paragraph rejection. Accordingly, the addition of claims 112, 113, 117, 127 and 128 to the heading of the 112, second paragraph, rejection, is not believed to be a new ground of rejection.

**(11) Response to Argument**

As discussed above in section 6 Issues, the prior art rejection over Asahi Shinbum, International Satellite Edition (London), November 28, 1986 (hereinafter, "the Asahi Shinbum article") is withdrawn in view of applicant's remarks.

It is believed that the withdrawn of the prior art rejection addresses each of applicant's remarks appearing at pages 7-51 and pages 114-173 of the Substitute Brief filed 1/18/00 (paper #89).

Additionally, as stated in section (10) Grounds of Rejection, note that the above 112, first paragraph, rejection has been modified in scope from the Final Office Action. Upon careful consideration of the evidence as a whole, including the specification teachings and examples, and applicant's affidavits and remarks, the examiner has determined that the instant specification is enabled for compositions comprising a transition

Art Unit: 1751

metal oxide containing an alkaline earth element and a rare-earth or Group IIIB element (as opposed to only compositions comprising  $Ba_xLa_{5-x}Cu_5O_y$ , as stated in the Final Office action). Applicant has provided guidance throughout the instant specification that various transition metal oxides (such as copper oxide) containing an alkaline earth element and a rare-earth or Group IIIB element result in superconductive compounds which may in turn be utilized in the instantly claimed methods.

With respect to the remaining claims rejected under 35 U.S.C. 112, first paragraph, all of appellant's remarks appearing at pages 52-101 of the Substitute Brief have been carefully considered. The following remarks are believed to address each of the issues raised by appellant in the Substitute Brief.

Applicants' arguments filed 1/18/00, as well as the Affidavits filed September 29, 1995, January 3, 1996 (paper nos. 49 and 52), as well as after-final submissions December 15, 1998: (1.132 Declarations of Mitzi, Tsuei, Dinger and Shaw) (Advisory mailed 2/25/99 (Paper 77E)) have been fully considered but they are not deemed to be persuasive.

The additional case law and arguments by the applicants have been duly noted. For the reasons that follow, however, the record as a whole is deemed to support the initial determination

Art Unit: 1751

that the originally filed disclosure would not have enabled one skilled in the art to make and use the invention to the scope that it is presently claimed.

The applicants quote several passages from their specification at pp. 13-15 of their September 29, 1995 Amendment, but the issue is the scope of enablement, not support. The present disclosure may or may not provide support for particular embodiments, but the issue here is the scope to which that disclosure would have taught one skilled in the art how to make and use a composition which shows the onset of superconductivity at above 26°K.

Construed in light of that issue, the invention is not deemed to have been fully enabled by the disclosure to the extent presently claimed.

(1) In their September 29, 1995 Amendment, the applicants argue that their disclosure refers to "the composition represented by the formula RE-TM-O, where RE is a rare earth or rare earth-like element, TM is a nonmagnetic transition metal, and O is oxygen", and list several species such as " $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ " which they indicate are found in the present disclosure.

(2) Notwithstanding that argument, it still does not follow that the invention is fully enabled for the **scope**

Art Unit: 1751

presently claimed. The claims include formulae which are much broader than the RE-TM-O formula cited in the disclosure. Claim 24 recites "a transition metal oxide", claim 88 "a composition", and claim 96 "a copper-oxide compound".

The present specification actually shows that known forms of "a transition metal oxide", "a composition", and "a copper-oxide compound" do **not** show the onset of superconductivity at above 26°K. At p. 3, line 20, through p. 4, line 9, of their disclosure, the applicants state that the prior art includes a "Li-Ti-O system with superconducting onsets as high as 13.7°K." Official Notice is taken of the well-known fact that Ti is a transition metal. That disclosure also refers to "a second, non-conducting CuO phase" at p. 14, line 18.

Accordingly, the present disclosure is not deemed to have been fully enabling with respect to the "transition metal oxide" of claim 24, the "composition" of claim 88, or the "copper-oxide compound" of claim 96.

The examples at p. 18, lines 1-20, of the present specification further substantiates the finding that the invention is not fully enabled for the scope presently claimed.

With a 1:1 ratio of (Ba, La) to Cu and an x value of 0.02, the La-Ba-Cu-O form (i.e., "RE-AE-TM-O", per p. 8, line 11) shows

Art Unit: 1751

"no superconductivity". With a 2:1 ratio of (Ba, La) to Cu and an x value of 0.15, the La-Ba-Cu-O form shows an onset of superconductivity at " $T_c = 26^\circ\text{K}$ ". It should be noted, however, that **all** of the claims in this application require the critical temperature ( $T_c$ ) to be "in excess of  $26^\circ\text{K}$ " or "greater than  $26^\circ\text{K}$ ".

The applicants also have submitted three affidavits attesting to the applicants' status as the discoverers of materials that superconduct  $> 26^\circ\text{K}$ . Each of the affidavits further states that "all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar manner (way)". Each of the affidavits add "(t)hat once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above  $26^\circ\text{K}$ , such a person of skill in the art, using the techniques described in the (present) application, which includes all known principles of ceramic fabrication, can make the transition metal oxide compositions encompassed by (the present) claims ...without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art." All three affiants apparently are the employees of the assignee of the present application.

Art Unit: 1751

Those affidavits do not set forth particular facts to support the conclusions that all superconductors based on the applicants' work behave in the same way and that one skilled in the art can make those superconductors without undue experimentation. Conclusory statements in an affidavit or specification do not provide the factual evidence needed for patentability.<sup>6</sup>

Those affidavits do not overcome the non-enablement rejection. The present specification discloses *on its face* that only certain oxide compositions of rare earth, alkaline earth, and transition metals made according to certain steps will superconduct at  $> 26^{\circ}\text{K}$ .

Those affidavits are not deemed to shed light on the state of the art and enablement *at the time* the invention was made. One may know *now* of a material that superconducts at more than  $26^{\circ}\text{K}$ , but the affidavits do not establish the existence of that knowledge on the filing date for the present application. Even if the present application "includes all known principles of ceramic fabrication", those affidavits do not establish the level of skill in the ceramic art as of the filing date of that application.

---

<sup>6</sup>See In re Lindner, 173 USPQ 356, 358 (CCPA 1972).



Art Unit: 1751

It is fully understood that the applicants are the pioneers in high temperature metal oxide superconductivity. The finding remains, nonetheless, that the disclosure is not fully enabling for the scope of the present claims.

The appellants quote a statement from part of the previous Office Action and asserts that the "Examiner does not support this statement with any case law citations." That assertion is incorrect. Seven decisions have been cited as providing the legal basis for this determination of non-enablement.<sup>7</sup>

The appellants further "note that the Examiner seemed to have specifically avoided applying (sic) the case law and, consequently, ... applicants take the Examiner's silence as concurrence in the manner that applicants have applied this case law." Apparently, the appellants are referring to their discussion<sup>8</sup> of the case law previously cited by this Examiner. Notwithstanding the appellants' commentary on case law, the April 15, 1997 Office Action, paper no. 54, sets forth the factual basis for the determination of non-enablement at pp. 5-10.

---

<sup>7</sup>See footnotes 1-4 in the April 15, 1996 Office Action, paper no. 54. See also, the corresponding sections of this Office Action.

<sup>8</sup>See pp. 12-25 of the September 29, 1995 Amendment, paper no. 50.

Art Unit: 1751

The appellants still further argues "that the Examiner does not rebut the case law and argument provided by applicants on (pages) 15-25 of their September 29, 1995 amendment which addresses (these issues) in detail." The point remains, nevertheless, that there appears to be a concurrence as to the applicable case law. That case law speaks for itself. What has been fully addressed in the previous Office Action and repeated above is the factual basis for the determination of non-enablement for the scope of the present invention.

The appellants argue that their own examples do not support the determination of non-enabling scope of the invention. Nevertheless, the record is viewed as a whole. If the applicants could not show superconductivity with a  $T_c > 26^\circ\text{K}$  for certain compositions falling within the scope of the present claims, it is unclear how someone else skilled in the art would have been enabled to do so at the time the invention was made.

The appellants assert that "(b)y the Examiner's statement that these (statements in the affidavits) are conclusionary (sic) the Examiner appears to be placing himself up as an expert in the field of superconductivity" and "respectfully request that the Examiner submit an affidavit in the present application rebutting the position taken by applicants' 3 affiants." Notwithstanding those assertions, this Examiner has determined that those

Art Unit: 1751

affidavits were insufficient because they were conclusory only, i.e., they lacked particular facts to support the conclusions reached.

The appellants argue that the "Examiner has provided no substantial evidence to support this assertion (of non-enabling scope of the invention). It is respectfully requested that the Examiner support (his) assertion with factual evidence and not unsupported statements." Nevertheless, the determination of non-enabling scope is maintained for the reasons of record.

The appellants argue that the "standard of enablement for a method of use is not the same as the standard of enablement for a composition of matter" and that their claimed invention is enabling because it is directed to a method of use rather than a composition. Basis is not seen for that argument, to the extent that it is understood. It is noted that 35 U.S.C. 112, first paragraph, reads as follows:

The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same, and shall set forth the best mode contemplated by the inventor of carrying out his invention.

Art Unit: 1751

Process of use claims also would be subject to the statutory provisions of 35 U.S.C. 112, first paragraph.

The appellants assert that the "Examiner has not shown by evidence not contained within applicants' teaching that the art of high  $T_c$  superconductors is unpredictable in view of applicants' teaching" (spelling and punctuation errors corrected). To the extent that the same assertion is understood, the rejection is maintained for the reasons of record.

The appellants point to "Copper Oxide Superconductors" by Charles P. Poole, Jr., et al., (hereinafter, "the Poole article") as supporting their position that higher temperature superconductors were not that difficult to make after their original discovery.

Initially, however, it should be noted that the Poole article was published *after* the priority date presently claimed. As such, it does not provide evidence of the state of the art at *the time* the presently claimed invention was made.

Moreover, the present claims are directed to processes of using metal oxide superconductors, **not** processes of making them. Even if the Poole article provided direct evidence of the state of the art at the time the invention was made, which it apparently does not, that evidence still does not pertain to the

Art Unit: 1751

issue at hand, namely, the process of using metal oxide superconductors to conduct electricity under superconducting conditions.

Finally, the Preface states in part at A3: "The unprecedented worldwide effort in superconductivity research that has taken place over the past two years has produced an enormous amount of experimental data on the properties of the copper oxide type materials that exhibit superconductivity above the temperature of liquid nitrogen. ... During this period a consistent experimental description of many of the properties of the principal superconducting compounds such as BiSrCaCuO, LaSrCuO, TlBaCaCuO, and YBaCuO has emerged. ... The field of high-temperature superconductivity is still evolving ..." That preface is deemed to show that the field of high-temperature superconductivity continued to grow, on the basis of on-going basic research, *after* the Bednorz and Meuller article was published.

The applicants submitted three affidavits, one each from Drs. Tsuei, Dinger, and Mitzi which were signed in May of 1998. Except for one change, those three affidavits are the same as the ones submitted before and discussed above.

Art Unit: 1751

Those affidavits have been changed to indicate that the present application "includes all known principles of ceramic fabrication known at the time the application was filed." However, that additional indication also is considered to be a conclusory statement unsupported by particular evidence.

Appellants have submitted three affidavits attesting to the applicants' status as the discoverers of materials that superconduct  $> 26^{\circ}\text{K}$ . Each of the affidavits states that "all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar manner (way)". Each of the affidavits add "(t)hat once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above  $26^{\circ}\text{K}$ , such a person of skill in the art, using the techniques described in the (present) application, which includes all known principles of ceramic fabrication, can make the transition metal oxide compositions encompassed by (the present) claims ...without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art.

It is the examiner's maintained position that while general principles of ceramic fabrication were most certainly known prior to the filing date of the instant application, the utilization of such techniques to produce superconductive materials within the

Art Unit: 1751

scope of the instant claims were not known. The affidavits are not effective to demonstrate enablement *at the time* the invention was made. As stated in paper #66, page 8, one may *now* know of a material that superconducts at more than 26K, but the affidavits do not establish the existence of that knowledge on the filing date of the present application.

It is acknowledged that applicants are pioneers in the filed of high temperature metal oxide superconductivity. The examiner respectfully maintains, for the reasons of record, that the disclosure is not fully enabling for the scope of the present claims.

With respect to the remaining claims rejected under 35 U.S.C. 112, second paragraph, all of appellant's remarks appearing at pages 102-113 of the Substitute Brief have been carefully considered. The following remarks are believed to address each of the issues raised by appellant in the Substitute Brief. Note that the Examiner declines to comment on appellants remarks regarding the after-final submissions which have not been entered or considered by the examiner.

The applicants argue that the terms "rare-earth like", "perovskite-like", and "perovskite-type" are definite. Those arguments are not found to be persuasive.

Art Unit: 1751

Each patent application is considered on its own merits. In some contexts it may have been clear in the art to use the term "like", such as when the "like" term is sufficiently defined. In the present case, however, the terms "rare-earth like" and "perovskite-like" are unclear. As suggested above, "rare-earth like" should be changed to -- rare earth or Group IIIB element --. The terms "like" or "type" also should be removed from "perovskite-like" or "perovskite-type".

This Examiner's Answer is deemed to be a complete discussion of all relevant issues raised by the appellants.




Art Unit: 1751

For the above reasons, it is believed that the rejections should be sustained.

Respectfully submitted,

Mark Kopec  
May 8, 2000

  
Mark Kopec  
Primary Examiner

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598

Filing:

Letter, Substitute Brief- Appeal to the Board of Appeals (3sets)

Certificate of mailing under 37 CFR 1.8 (a)

Date of Deposit: January 13, 2000

PLEASE STAMP & RETURN TO US

TRANSITION.....

in re application of: J. Bednorz et al

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH

Serial No. 08/303,561; Docket No. X0987-074BY Atty.: DPM

Received in the U.S. Patent & Trademark Office:

No. of pages of specification:       ; No. of pages of claims       

No. of sheets of drawings:       

Declaration is attached to specification.

All fees are charged to our Account No. 09-0468

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of: J. Bednorz et al.

Docket No.: YO987-074BY

Serial No: 08/303,561

Group Art Unit: 1751

Filed: 09/09/94

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

Assistant Commissioner for Patents  
Washington, D.C. 20231

**CERTIFICATE OF MAILING UNDER 37 CFR 1.8 (a)**

I hereby certify that the attached correspondence comprising:

Letter

Substitute Brief - Appeal to the Board of Appeals (3 sets)

Acknowledgment Card

is being deposited with the United States Postal Service as first class mail in an envelope addressed to:

**Assistant Commissioner for Patents  
Washington, D.C. 20231**

on January 13, 2000

Daniel P. Morris

(Type or printed name of person mailing paper or fee)

  
(Signature of person mailing paper or fee)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/303,561

Filed: 09/09/94

For: New Superconductive Compounds Having High Transition  
Temperatures, Methods For Their Use and Preparation

Date: January 13, 2000

Group Art Unit: 1751

Examiner: M. Kopec

Assistant Commissioner for Patents  
Washington, D. C. 20231

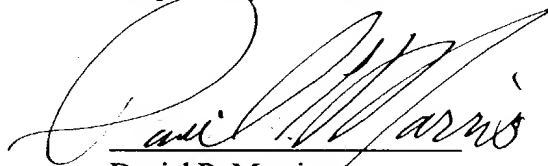
**LETTER**

In response to the Office Letter dated September 13, 1999 please consider the following:

Enclosed is a substitute brief including the changes requested by the Examiner and the changes made by Applicant's Amendment to Appeal Brief dated September 1, 1999.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

Respectfully submitted,



Daniel P. Morris  
Reg. No. 32,053  
(914) 945-3217

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Date: January 13, 2000

Applicants: Bednorz et al.

Docket: YO987-074BY

Serial No.: 08/303,561

Group Art Unit: 1751

Filed: 09/09/94

Examiner: M. Kopec

For: New Superconductive Compounds Having High Transition  
Temperatures, Methods For Their Use and Preparation

Assistant Commissioner for Patents  
Washington, D. C. 20231

**SUBSTITUTE BRIEF**

**APPEAL TO THE BOARD OF APPEALS AND INTERFERENCE'S**

Sir:

Applicants hereby appeal, Pursuant to 37 C.F.R. 1.192(c), the Examiner's final rejection  
of Claims as set forth in the:

Five Advisory Actions dated February 25, 1999; and  
Final Office Action dated June 25, 1998

**REAL PARTY IN INTEREST**

The above-identified patent application has been assigned to the International  
Business Machines Corporation. The assignment has been recorded in the U.S. Patent  
and Trademark Office: Recordation date January 9, 1995; Reel/Frame 7331/0519.

## **RELATED APPEALS AND INTERFERENCES**

There are no related appeals and interferences.

Co-pending US application serial number 08/479,810 filed on June 7, 1995 is a division of the present application.

## **STATUS OF CLAIMS**

Claims 24-26, 86-90 and 96-177 are presently pending in the present application.

Claim 136 is allowed. Claims 24-26, 86-90, 96-135 and 137-177 have been finally rejected in the Office Action dated June 25, 1998 which provides the basis for this appeal.

The following table lists the independent claims and the claims which depend therefrom:

Set	Independent Claim	Dependent Claim
1	24	25, 26
2	86	87
3	88	90
4	96	97-102
5	103	104-108
6	109	
7	110	
8	111	
9	112	
10	113	
11	114	
12	115	
13	116	
14	117	
15	118	
16	119	
17	120	
18	121	
19	122	
20	123	
21	124	
22	125	
23	126	
24	127	
25	128	
26	129	164
27	130	165
28	131	166
29	132	167
30	133	168
31	134	169
32	135	170
33	136	171
34	137	172
35	138	173
36	139	174
37	140	175
38	141	176
39	142	177
40	143	144

## STATUS OF AMENDMENTS

On November 27, 1997, applicants submitted an amendment under 37 CFR 1.129(a) in response to the final rejection dated August 27, 1997. On May 14, 1997, applicants filed a supplementary response to the final rejection dated August 27, 1997. In response to these two submissions under 37 CFR 129(a), all pending claims except for claim 136 were finally rejected in the Final Action dated June 25, 1998. Applicants filed a notice of Appeal on December 28, 1998.

In the response to the Final Action dated June 25, 1998, applicants submitted the following Amendments after final rejection:

Amendments After Final Rejection:

November 25, 1998: Not entered (Advisory mailed 12/14/98 (Paper #68))

December 10, 1998: Not entered (Advisory mailed 2/25/99 (Paper 77C))

December 11, 1998: Not entered (Advisory mailed 2/25/99 (Paper 77A))

December 15, 1998 (2): [1.132 Declarations of Mitzi, Tsuei, Dinger and Shaw]  
Entered (Advisory mailed 2/25/99 (Paper 77E))

December 15, 1998: [1.132 Declaration of James Leonard]  
Not entered (Advisory mailed 2/25/99 (Paper 77B))

December 18, 1998: Entered (Advisory mailed 2/25/99 (Paper 77E))

December 22, 1998: Not entered (Advisory mailed 2/25/99 (Paper 77A))

December 27, 1998: Not entered (Advisory mailed 2/25/99 (Paper 77D))

June 14, 1999: Entered (Advisory mailed 7/8/99 (Paper #83))

June 15, 1999 (2): Entered (Advisory Actions mailed 7/8/99 (Paper #84 and #85))

June 27, 1999: Not entered (Advisory mailed 7/8/99 (Paper #86))



In response the five Advisory Actions dated February 25, 1999 were received by Applicants. In response to these Advisory Actions three Amendments of the Final Rejection were submitted on June 14, 1999; June 15, 1999 and June 15, 1999. By telephone conversation the Examiner told applicants that these would be entered.

On June 24, 1999, Applicants resubmitted the amendment after final dated December 27, 1998 which the Examiner told the undersigned attorney was not received.

### **SUMMARY OF THE INVENTION**

A method of flowing a superconducting electrical current in a transition metal oxide having a  $T_c$  greater than  $26^\circ\text{K}$  and maintaining the transition metal oxide at a temperature less than said  $T_c$ .

In a more particular aspect of the method of the present invention the transition metal is copper.

In another more particular aspect of the method of the present invention the transition metal oxide has a perovskite-like or a perovskite-type crystal structure which is a perovskite or near perovskite structure.

In another more particular aspect of the present invention the transition metal oxide has a layered-like or layered-type structure.

In another more particular aspect of the present invention, the composition includes a transition metal, a rare or rare earth like element, an alkaline earth element and oxygen.

### **ISSUES**

1. Are claims 24-26, 86-90, 96-135 and 137-177 supported by the priority document?
2. Are claims 24-26, 86-90, 96-135 and 137-177 anticipated under 35 USC 102(a) by the Asahi Shinbum article?
3. Are the claims 24-26, 86-90, 96-135 and 137-177 obvious under 35 USC 103(a) in view of the Asahi Shinbum article?
4. Are claims 24-26, 86-90, 96-113, 129-131, 134, 135, 139-142, 143-163, 164-166, 169, 170, and 174-177 not enabled under 35 USC 112, first paragraph.
5. Are claims 86-87, 96-108, 115, 118, 120, 122, 123, 124, 129-135, 137-142, 164-169, and 170-177 indefinite under 35 USC 112, second paragraph.

### **GROUPING OF THE CLAIMS**

Each claim is appealed individually.

## **ARGUMENT**

### **Priority**

The Examiner has acknowledged applicant's claim for priority under 35 USC §119 in the parent application, Serial No. 08/053,307 filed April 23, 1993. The certified copy has been filed in parent application, Serial No. 08/053,307, filed on April 23, 1993 as paper no. 28. (References to the priority document herein are to the corresponding European Patent Application 275 343 A1 published on July 27, 1988.)

Applicants respectfully disagree with the Examiner that support is not found in that certified copy for the invention as presently claimed.

In this regard the Examiner states:

Applicants' arguments filed April 11, 1996, January 3, 1996 and September 29, 1996, paper numbers 53, 50 and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996, paper numbers 49 and 52, have been fully considered but they are not deemed to be persuasive. The applicants quote some passages out of the priority document and argue that the present claims are fully based on that document. Nevertheless, that priority document is not deemed to provide basis for the limitations found in the present claims.

In this passage the Examiner states that "Applicants' arguments ... are not **deemed** to be persuasive" and "[n]evertheless, that priority document is not **deemed** to provide basis for the limitations found in the present claims." Webster's Ninth New Collegiate Dictionary (Merriam-Webster Inc., Springfield, Mass. 1987) defines "deem" as a transitive verb meaning "to come to think or judge" and as an intransitive verb meaning "to have an opinion : believe." The examiner has used the intransitive form of the verb "deemed". The examiner has cited no statutory or case law authority which permits an examiner to object to a claim of priority based on the examiners "opinion" or "belief" that a priority document does not support applicant's claims. The Examiner must support a denial of a claim of priority based on what is actually stated in the priority document.

The examiner further states in support of the examiner's "opinion" or "belief" at page 3, paragraph 4.b;

- i. The recitation of a "composition including a transition metal, a rare earth or rare earth-like element, an alkaline earth element, and oxygen", as found in claim 86 (lines 2-4). The certified priority document may provide basis for the formula  $RE_2TM.O_4$  at p. 2, para. 4, but the claimed composition is deemed to be much broader than that formula.

Applicants respectfully disagree. In the priority document, for example in the abstract, RE is a rare earth element, TM is a transition metal and O is oxygen. The priority document further states at Col. 2, lines 22-25 "the lanthanum which belongs to the IIB group of elements is in part substituted by one member of the neighboring IIA group of

elements...". Group IIA elements are the alkaline earth elements. The present specification teaches at page 11, lines 22-23, that RE stands for the rare earths (lanthanides) or rare earth-like elements. The "rare earth like element" act like a rare earth element in the superconductive composition. Thus a rare earth-like element is an equivalent of rare earth element. Similar language appears in the present specification at page 12 lines 6--8, "the lanthanum which belongs to the IIB group of elements is in part substituted by one member of the neighboring IIA group of elements ...". Therefore, the priority document teaches a "composition including a transition metal, a rare earth or rare earth-like element, and alkaline earth. Applicants note that in the passage quoted above, the Examiner incorrectly states that applicants claim a composition. This is not correct. Applicants claim a method of flowing a superconducting current in a transition metal oxide. In the last sentence of the passage quoted above the Examiner incorrectly states "the claimed composition is **deemed** to be much broader than [the] formula"  $RE_2TM.O_4$ ". The priority document is not limited to his formula. The composition taught by the priority document have variable amounts of oxygen, rare earth, rare earth-like and alkaline earth elements as is clearly shown in the abstract of the priority document.

The Examiner further states:

- ii. The limitation "non-stoichiometric amount of oxygen", as found in claim 6 and 86 (line 6). Basis may be seen for an oxygen deficit at p. 2, para. 4, but no such basis is seen for the more general limitation of "a nonstoichiometric amount of oxygen".

Applicants respectfully disagree. At Col. 3, lines 46-50 the priority document refers to applicants publication in Z. Phys. B - Condensed Matter 64 (1986) 189-193 which is incorporated by reference in the present specification at page 6, lines 7-10. (This article is referred to here in as Applicants' article.) This article states at page 190, left col., lines 13-14 "[t]his system exhibits a number of oxygen-deficient phases with mixed-valent copper constituents." The priority document has various general formulas such as at Col. 3, lines 40, " $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$   $x < 1$  and  $y \geq 0$ ." The abstract has a more generic formula. A stoichiometric compound has a fixed amount of each element that make up the compound. Since, the amount of oxygen is variable, the formula has nonstoichiometric amounts of oxygen. Therefore, the priority document teaches nonstoichiometric amounts of oxygen.

In attachment A of this appeal, there are copies of pages 245 and 225 of Inorganic Chemistry by Moeler, John Wiley & Sons, Inc. 1952 and a copy of page 70 of Fundamentals of Chemistry, A Modern Introduction by Brescia et al. , Academic Press, 1966. Attachment A provides an explanation of the terms stoichiometric and nonstoichiometric. The documents in Attachment A support applicants position that the priority document teaches nonstoichiometric amounts of oxygen.

The Examiner further states:

- iii. The limitation "a composition exhibiting a superconductive state" is found in present claim 88, (line 2). Wherein the certified priority document

may provide basis for compositions of the formula  $\text{RE}_2\text{TM.O}_4$ , as discussed above, but "transition metal oxide" and "superconductive state" are deemed to be much broader than the formula  $\text{RE}_2\text{TM.O}_4$ .

Applicants respectfully disagree. The field of the invention of the priority document is "a new class of superconductors in particular components ..." and the title is "New Superconductive Compounds ...". Applicants' article which is referred to in the priority document states at page 190, left Col., lines 14-16 from the bottom "X-ray powder diffractograms ... revealed three individual crystallographic phases." In the conclusion at page 192 the article states "[t]he system consists of three phases, one of them having a metallic perovskite-type layer-like structure. The characterization of the new, apparently superconducting, phase is in progress." Thus the priority document supports the limitation "a composition exhibiting a superconductive state". The general formula  $\text{RE}_{2-x}\text{AE}_x\text{TM.O}_{4-y}$   $x < 0.3$   $0.1 \leq y \leq 0.5$  and the more specific formula  $\text{RE}_2\text{TM.O}_4$  of the priority document is a composition; is a metal oxide; and is a transition metal oxide as recited in claims 24, 89 and 90. As noted above, the Examiner incorrectly implies that the priority document is limited to compounds having the formula  $\text{RE}_2\text{TM.O}_4$ .

The Examiner further states:

- iv. The limitation "a copper-oxide compound" is recited in claim 96 (line 6).
- 6). The certified priority document may provide basis for compositions of the formula  $\text{RE}_2\text{TM.O}_4$ , as discussed above, but "a copper-oxide

compound" is not deemed to be equivalent to a composition of the formula  $RE_2TM.O_4$ . Basis is not seen in the certified priority document for "a copper oxide compound" with the breadth of the present claims.

Initially the Examiner incorrectly implies claim 96 is directed to a copper oxide compound. Claim 96 is directed to a "copper oxide composition consisting essentially of a copper oxide compound having a layer-type perovskite-like structure."

Applicants respectfully disagree. The priority document recites numerous copper oxide compositions. It is noted that the Abstract of the priority document refers to "[t]he superconductive compounds are oxides of the general formula  $RE_{2-x}AE_xTM.O_{4-y}$ , wherein RE is a rare earth, AE is a member of the group of alkaline earths or a combination of at least two members of that group, and TM is a transition metal, and wherein  $x < 0.3$  and  $0.1 \leq y \leq 0.5$ ." This formula permits no alkaline earth and a varying amount of alkaline earth, rare earths and a varying amount of oxygen. At column 3, lines 20 and 35, there is recited "the Ba-La-Cu-O system" and at line 41 " $La_{2-x}Ba_xCuO_{4-y}$   $x < 1$  and  $y \leq 0$  and at line 44 teaches  $La_{1-x}Va_xCuO_{3-y}$ . Thus the priority document provides support for a composition including a transition metal, a rare earth or rare earth-like elements, an alkaline earth element, an oxygen as found in applicants' claim, specifically claim 86. It is noted that at column 2, lines 13-19 the priority document states that "it is a characteristic of the present invention that in the compounds in question that the RE portion is partially substituted by one member of the alkaline earth group of metals, or by a combination of the members of this alkaline earth group and that the oxygen content is at a deficit." It is further noted that at



column 2, lines 20-23 it states that "for example, one such compound that meets the description given by this lanthanum copper oxide  $\text{La}_2\text{CuO}_4$  in which the lanthanum which belongs to the IIIB group of the elements is in part substituted by one member of the neighboring IIIA group of elements."

The priority document at column 3, line 6 recites Ti as a transition metal. It is noted that in claim 1 of the priority document, claim 1 recites the structure  $\text{RE}_{2-x}\text{AE}_x\text{TM.O}_{4-y}$  wherein TM is a transition metal. Claim 2 therein recites copper as the transition metal. Claim 3 therein recites nickel as the transition metal. Claim 8 therein recites chromium as the transition metal. Consequently, a broader class of transition metals other than copper is supported by the priority document.

It is clear from the quoted sections of the priority document that the priority document clearly supports a much broader composition than the Examiner is claiming that it does, and that the priority document, in fact, does support applicant's claims.

As noted above, the general formula of the priority document is much broader than the formula  $\text{RE}_2\text{TM.O}_4$  which the Examiner incorrectly states the priority document is limited to. The quantity of oxygen, the rare earth element and of an alkaline element is variable and the transition metal is not limited to copper. Consequently, the term "a copper-oxide compound" is adequately supported by the priority document.

The Examiner further states:

v. The limitation to the effect that "the copper oxide compound includes (including) at least one rare-earth or rare-earth-like element and at least one alkaline-earth element", as recited in claim 103 (lines 6 and 8). The certified priority document may provide basis for compositions of the formula  $RE_2TM.O_4$ , as discussed above, but basis is not seen for the more general limitation of "a copper-oxide compound" with a rare-earth (like) element and an alkaline earth element.

Applicants respectfully disagree. The second line of the abstract gives the general formula " $RE_{2-x}AE_xTM.O_{4-y}$   $x < 0.3$  and  $0.1 \leq y \leq 0.5$ ." In claim 1 of the priority document  $y \leq 0.5$ . Claim 2 recites RE is lanthanum and TM is a copper. Claim 3 recites RE is cerium and TM is nickel. Claim 4 recites RE is lanthanum and TM is nickel. Claim 8 recites RE is lanthanum and TM is chromium. Claim 9 recites RE is neodymium and TM is copper. Applicants' claim 103 recites "the copper-oxide compound including at least one rare-earth or rare-earth-like element and at least one alkaline-earth element". The priority document clearly supports this recitation. Applicants, as stated above, respectfully submit the Examiner is misrepresenting the priority document which refers throughout and, in particular, in the Abstract to "the general formula  $RE_{2-x}AE_xEM.O_{4-y}$  as stated above which includes a copper-oxide as stated above. The Examiner further states in the passage quoted above "but basis is not seen for the more general limitation of 'a copper-oxide compound' with a rare-earth (like) element and in alkaline earth element." It is noted that in the priority document, claim 2 refers to lanthanum as

the rare earth; claim 3 refers to cerium as the rare earth; claim 5 refers to barium as a partial substitute for the rare earth; claim 6 refers to calcium as a partial substitute for the rare earth; claim 7 refers to strontium as a partial substitute for the rare earth and claim 9 refers to neodymium as the rare earth. Clearly, the priority document uses barium, calcium and strontium. Consequently, the priority document supports the term rare earth-like since it includes elements (e.g. barium, calcium and strontium) other than those commonly referred to as the rare earth elements [which are elements 57-71] which satisfy the teaching of the priority document and of the present application. The Abstract of the priority document refers to "AE as a member of the alkaline earth or a combination of at least two members of that group". Consequently, the priority document clearly supports an alkaline earth element.

The Examiner further states:

vi. The limitation to the effect that "the copper-oxide compound includes at least one element (oxygen) in a nonstoichiometric atomic proportion", as found in claim 101 (lines 2 and 3), 102 (lines 2 and 3), 107 (lines 2 and 3), and 108 (lines 2 and 3). Basis may be seen for an oxygen deficit as discussed above, but no such basis is seen for the more general limitation of "a nonstoichiometric atomic proportion".

Applicants disagree for the same reasons given above for why the priority document supports "nonstoichiometric amount of oxygen".

The Examiner further states:

vi. The limitation as to "the effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$ , as found in claim 103 (lines 13, 6 and 17). The critical temperature,  $T_c$ , is discussed throughout that certified priority document, but not  $T_{\rho=0}$ .

Applicants respectfully disagree.  $T_{\rho=0}$  is the temperature at which the bulk resistivity is about zero.  $T_c$  is the critical temperature or the temperature above which superconductivity does not exist. The priority document refers to applicants' article of which Figures 1,2 and 3 are the same figures as Figures 2, 3 and 4 of the present application. At page 22, lines 19-24, the present specification refers to Figure 4 of the specification stating "[i]ts resistivity decreases by at least three orders of magnitude, giving evidence for the bulk being superconducting below 13 K with an onset around 35 K, as shown in FIG. 4 on an expanded scale." When a superconductor is totally superconductive the resistivity,  $\rho$ , is zero. The temperature at which this occurs is  $T_{\rho=0}$ . Applicants' article, (and thus the priority document), at page 191, right column, in referring to Fig. 1 thereof states "[u]pon cooling from room temperature, the latter exhibit a nearly linear metallic decrease of  $\rho(T)$ , then a logarithmic type of increase, before undergoing the transition to superconductivity." And in the sentence bridging pages 191-192 "[t]herefore, under the above premises, the peak in  $\rho(T)$  at 35 K, observed ... has to be identified as the start to superconductive cooperative

phenomena." And Applicants' article at page 192, left column, states "[u]pon cooling below  $T_c$  ... the bulk resistivity gradually drops to zero by three orders of magnitude, for sample 2( Fig. 1)" From these statements in applicants article (which is referred to in the priority document) it is clear that the language objected to by the examiner is supported in the priority document.

In response to Applicants' arguments filed March 7, 1997 (#59) the Examiner states "they have been fully considered but not found to be persuasive".

The Examiner states:

i. The applicants quote portions out of the priority document and assert that those quoted sections "clearly (support) a much broader composition than the Examiner is claiming it does, and that the priority document, in fact, does support applicant's (sic) claim 86." The fact remains, nevertheless, that the priority document refers to the general formula  $RE_2TM.O_4$  in which the rare earth element (RE) may be partially substituted with a Group IIA metal. That disclosure in the priority document does not provide support for the broader limitations of the present claims, which do not limit the invention to that general formula.

As state above the Examiner incorrectly states that the priority document is limited to formula  $RE_2TM.O_4$ . This is clearly incorrect.

The Examiner further states:

ii. The applicants argue that the disclosure of varying amounts of oxygen in the priority document provides support for earlier priority for the term "non-stoichiometric amount of oxygen". Again, however, that disclosure in the priority document does not provide support for the broader limitations of the present claims, which do not limit the invention to those varying amounts.

It is not clear what the Examiner is trying to say in the last sentence of this quoted passage. The general formula in the Abstract of the priority document,  $RE_{2-x}AE_xTM.O_{4-y}$ , has the atomic amount of O varying from 0 to 4 independent of the atomic amount of RE, AE and TM. Thus the amount of O must have non-stoichiometric values. The Examiner's comments in the passage above are clearly in error.

The Examiner further states:

iii. The applicants urge that the disclosure in the priority document of the formula  $RE_2TM.O_4$  provides support for their limitations of "transition metal", "copper-oxide compounds", "rare earth or rare earth-like elements", and "alkaline earth element". Again, however, that disclosure in the priority document does not provide support for the broader

limitations of the present claims, which do not limit the invention to that formula.

The Examiner again incorrectly states that the priority document is limited to the formula  $\text{RE}_2\text{TM.O}_4$ . As stated above the examiner is clearly in error. The priority document supports a much broader formula than  $\text{RE}_2\text{TM.O}_4$ . As shown above, the priority document clearly supports applicants' claim limitations "transition metal", "copper-oxide compounds", "rare earth or rare earth-like elements" and "alkaline earth elements".

The Examiner further states:

iv. The applicants further "assume that the Examiner agrees with applicant's (sic) statements in their prior response in that the concept of the intercept temperature is well known in the prior art and can be included in claim 103." No basis is seen for that assumption. As noted in the previous Office Action and repeated above, the term " $T_{\rho=0}$ " is not found in the priority document. Well known or not, there is no basis for that term in the priority document.

For the reason given above the priority document clearly supports the term " $T_{\rho=0}$ ". Although this particular symbol is not used in the priority document, the priority document clearly shows that as temperature is decreased the resistivity of a

superconductor begins to drop in the value at the critical temperature  $T_c$  and goes to zero at another temperature, that is  $T_{\rho=0}$ . This symbol is just a short hand notation for that temperature. This property of superconducting materials is well known prior to applicants filing date, in fact that is what is meant by the term superconductor which is a material for which  $\rho=0$  for temperatures less than a certain temperature, i.e.,  $T_{\rho=0}$ . It is also well-known that: "[i]n the ideal case the resistance vanishes completely and discontinuously at a transition temperature.  $T_s$  ... Actually, the resistance temperature curve does fall more sharply the more specimen is like a single crystal ... [T]he drop always occurs in a measurable temperature range ..." (Theory of Superconductivity, M. von Laue, Academic Press, Inc., 1952) (See Appendix C of Applicants' response dated September 25, 1995). Moreover, the priority document at column 1, the first sentence of the Background of the Invention states "[s]uperconductivity is usually defined as the complete loss of electrical resistance of a material at a well defined temperature". That temperature is symbolically represented as  $T_{\rho=0}$ .



## CLAIM REJECTIONS - 35 USC § 102

Claims 24-26, 86-90, 96-135, and 137-177 have been rejected under 35 U.S.C. § 102(a) as being anticipated by Asahi Shinbum, International Satellite Edition (London), November 28, 1986 (hereinafter, "the Asahi Shinbum article").

The Examiner is stating that everything within applicants non-allowed claims is found in the Asahi Shinbum article. All of Applicants' non-allowed claims are dominant to (or generic to) the one allowed claim, claim 136. Thus by stating that all the non-allowed claims are anticipated, the Examiner is stating that the portion of each non-allowed claim which does not overlap the allowed claim is taught in the Asahi Shinbum article. This means that a person of skill in the art needs nothing more than what is taught in the Asahi Shinbum article to practice that part of each of Applicants non-allowed claims which does not overlap Applicants' allowed claim.

The only parts of the Asahi Shinbum article which are relevant to applicants claim are in the first paragraph:

A new ceramic with a very high  $T_c$  of 30K of the superconducting transition has been found. The possibility of high  $T_c$  - superconductivity has been reported by scientists in Switzerland this spring. The group of Prof. Shoji TANAKA, Dept. Appl. Phys. Faculty of Engineering at the University of Tokyo confirmed in November, that this is true.

in the second paragraph:

The ceramic newly discovered, is an oxide compound of La and Cu with Barium which has a structure of the so-called perovskite and shows metal-like properties. Prof. Tanaka's laboratory confirmed that this material shows diamagnetism (Meisner effect) which is the most important indication of the existence of superconductivity.

The Swiss scientist are the inventors of the present application. Thus this clearly refers to applicants work which was reported in Applicants article. These passages say that Prof. Tanaka confirmed applicants work. The newly discovered ceramic referred to in the article is the ceramic reported on in Applicants' article. The present applicant was filed less than one year after the publication of applicants' article. This article is a disclosure of Applicants' own invention and cannot be used as a reference against the present application.

Since the present application was filed within one year of Applicants' article, Applicants' article is not a reference as to them. Thus the only portion of the Asahi Shinbum article relevant to Applicants' claims is:

A new ceramic with a very high  $T_c$  of 30K of the superconducting transition ... is an oxide compound of La and Cu with Barium which has a structure of the so-called perovskite and shows metal-like properties.

Since the Asahi Shinbum article refers to " $T_c$  of 30K" and since each of Applicants claims recites  $T_c > 26$  °K, the Asahi Shinbum article alone cannot anticipate  $T_c > 26$  °K since to be an anticipation a reference must contain all the limitations of the claim it is said to anticipate. Also, the Asahi Shinbum article provides no teaching of how to made the "new ceramic". A reference which does not provide a method of making a composition cannot anticipate a claim to the composition and thus to a use of that new composition. Also, the Asahi Shinbum article has no specific embodiment of the new composition. Thus it cannot anticipate under 35 USC 102.

### **Applicants' Article Was in the US in Ready To File Form**

The issue involved here is straight forward. A third party reproduced and reported that fact in a written publication before of Applicants' filing date. The work of Applicants was reported in a written description published before the publication of the third party. Applicants filed the present application within one year of their publication, but after the third party publication. If Applicants did not file the present applicant within one year of the date of Applicants' article, Applicants' article would be a valid reference under 35 USC 102(a). But since Applicants filed the present application within 1 year of Applicants' article, it is not a reference under 35 USC 102(b).

35 USC 100 states the term "invention" means invention or discovery.

35 USC 102(a) states "[a] person shall be entitled to a patent unless ... the invention was known or used by others in this country, or patented or described in a printed publication in this or a foreign country, before the invention thereof by the applicants for patent."

Applicants invention or discovery was on or before April 17, 1986 which is the date Applicants submitted Applicants' article to Z.Phys.B. That article was published in September, 1986. Therefore, Applicants invented their invention prior to the date of the Asahi Shinbum article, November 28, 1986. Evidence submitted proving that applicants conception was in the United States at applicants direction prior to Nov. 28, 1986 is discussed below. In addition, the following evidence shows that Applicants' article was in this country in possession of IBM, the assignee, prior to the date of the Asahi Shinbum article. Attachment K of Applicants' response dated December 27, 1998, page 1, is a copy of the front cover of Zeitschrift Fur Physik B Condensed Matter Vol. 64 which contains Applicants' article ( pp 189-193) which is referred to and incorporated by reference at page 6, lines 6-10, of Applicant's specification. Applicants state at page 6 of the specification that Applicants' article is "[t]he basis or our

invention". This page bears in the upper right the date stamp of the IBM Research Library bearing the date of Sept. 18, 1986. Page 2 of Attachment K of Applicants' response dated December 27, 1998, is an enlarged view of the upper right corner showing the date stamp. Thus the assignee of the present invention, IBM, who was the employer of the inventors at the time of the conception of the invention, had in its possession in the United States, prior to the date of the Asahi Shinbum, a copy of the article which Applicants state forms the basis of their invention. Thus IBM had in its possession in the United States a written description of applicants' invention in "ready to patent form" ( as defined by the United States Supreme Court in Pfaff v. Wells 48 USPQ 2d 1641 decided November 10, 1998) prior to the date of the Asahi Shinbum article. The US Supreme Court held that "reduction to practice" is not needed to establish a date for invention. The court stated " [t]he statute's only specific reference to that term is found in §102(g), which sets fort the standard for resolving priority between two competing claimants to a patent." Since §102(g) is not applicable here, "diligence" and "reduction to practice" are not required. Applicants article in Zeitschrift Fur Physik "is proof that prior to [the date of the Asahi Shinbum article applicants have] prepared drawings or other descriptions of the invention that were sufficiently specific to enable a person skilled in the art to practice the invention." The Asahi Shinbum article sates that applicants' work was reproduced, by others, thus applicants article was sufficiently specific for a person of skill in the art to practice applicant s' invention. Also, as stated in Applicants' response dated December 18, 1998, more than 5,200 articles refer to applicants article showing that applicants enabled the field of high  $T_c$  superconductivity. Thus the Asahi Shinbum article is not a valid §102(a) reference against Applicants' claimed invention.

The Examiner states:

- ii. The applicants assert that the Asahi Shinbum article reports a third party's confirmation of their original discovery. That assertion appears to be correct, but the article still is deemed to be prior art under 35 USC 102(a).

(1) It should be noted again, however, that the applicants' discovery was not originally made in this country- and that they cannot show an earlier date than December 1986 for their invention in this country. The Asahi Shinbum article was published on November 28, 1986.

Applicants disagree with the Examiner. Applicants note that the Examiner acknowledges that the Asahi Shinbum article "confirms [Applicants'] original discovery." 35 USC 102(a) does not require applicants to show a date of invention in this country prior to the Asahi Shinbum article to avoid the Asahi Shinbum article being prior art. 35 USC 102(a) states "A person shall be entitled to a patent unless ... the invention was ... described in a printed publication in this or a foreign country, before the invention thereof by the application for patent." 35 USC 100 does not include reduction to practice in this country or conception in this country as part of the definition of invention. Only 35 USC 102(g) includes the language "reduction to practice" and "invention in this country". If Congress intended a reduction to practice to be necessary for a patent applicant to show that they invented their invention before the date of the printed publication, Congress would have included such language in the 35 USC 102(a). Also, if Congress intended that invention in this country was to be necessary for a patent applicant to show that they invented their invention before the date of the printed publication, Congress would have included such language in 35 USC 102(a).

In the final rejection the Examiner states:

- a. As discussed in paper no. 20 of the ancestral application, 07/053,307, it is not fully clear to what exact date applicants are entitled. Based on the record, nonetheless, that date would appear to be no later

than around December 13, 1986, the date samples were tested in the US to show superconductivity. See MPEP 715 et seq. The Asahi Shinbum article was published on November 28, 1986.

b. The reference confirms superconductivity in an oxide compound of La and Cu with Ba having a structure of the so-called perovskite structure. Although the reference fails to teach use of the testing of zero resistance for confirming superconductivity, it inherently must have been used because it is one of two methods used for testing for superconductivity (the other being diamagnetism). Accordingly, the burden of proof is upon the applicants to show that the instantly claimed subject matter is different from and unobvious over that taught by this reference."

In response to applicants' arguments filed April 11, 1996, January 3, 1996, and September 29, 1995, paper nos. 53, 50, and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996, paper nos. 49 and 52, the Examiner states they "are not **deemed** to be persuasive", that is it is the Examiner's **opinion** that they are not persuasive.

The Examiner cites In re Brown, 173 USPQ 685, 688; In re Best, 195 USPQ 430; and In re Marosi, 218 USPQ 289, 293 to support his rejection. These decisions are not directed to whether a reference is a valid §102(a) reference and are thus not relevant to this issue.

The Examiner is using Asahi Shinbum as a reference under 35 USC §102(a). Applicants disagree that this is proper since to do so does not permit applicants the one

year period provided under 35 USC §102(b) to file a US application after their own publication. The one year period permitted applicants to file the present application up to September 1987. The date of the Asahi Shinbum article November 28, 1986 is after the date of applicants' publication, but before the end of the one year.

Applicants believe that the Examiner has incorrectly applied 35 USC §102(a). The Court of Custom and Patent Appeal in *In re Katz* 215 USPQ 14, 17 states that:

It may not be readily apparent from the statutory language that a printed publication cannot stand as a reference under §102(a) unless it is describing the work of another. A literal reading might appear to make a prior patent or printed publication 'prior art' even though the disclosure is that of the applicant's own work. However, such an interpretation of this section of the statute would negate the one year period afforded under §102(b) during which an inventor is allowed to perfect, develop and apply for a patent on his invention and publish descriptions of it if he wishes.

Thus, one's own work is not prior art under §102(a) even though it has been disclosed to the public in a manner or form which otherwise would fall under §102(a). Disclosure to the public of one's own work constitutes a bar to the grant of a patent claiming the subject matter obvious therefrom only when the disclosure occurred more than one year prior to the date of the application, that is, when the disclosure creates a one-year time bar, frequently termed a "statutory bar," to the application under

§102(b). As stated by this court in *In re Facius*, 56 CCPA 1348, 1358, 408 F.2d 1396, 1406, 161 USPQ 294, 302 (1969), "But certainly **one's own invention, whatever the form of disclosure to the public, may not be prior art against oneself, absent a statutory bar.**" [Emphasis in original].

The Asahi Shinbum article states in the first paragraph, "The possibility of high T, superconductivity has been reported by scientists in Switzerland this spring". The "scientists in Switzerland" are the inventors of the present application. Applicants' invention was reported in Applicants' article which was submitted for publication in the Spring of 1986. The Asahi Shinbum article only reports the work of applicants and that it was reproduced by Prof. Tanaka. This article is a disclosure of applicants' "own invention" and cannot be used as a reference. Therefore, the Examiner is in error in rejecting Applicants claims 24-26, 86-90, 96-135 and 137-177 under 35 USC §102(a) as anticipated by Asahi Shinbum and under 35 USC §103 as obvious over Asahi Shinbum.

In regard to the two-year grace period under a prior statute corresponding to 35 USC §102(b) the U.S. Supreme Court in *Andrews v. Hovey*, 123 US 267 (1887) states that:

"The evident purpose of the section was to fix a period of limitation which should be certain, and require only a calculation of time, and should not depend upon the uncertain question of whether the Applicant had consented to or allowed the sale or use. Its object was to require the



inventor to see to it that he filed his application within two years from the completion of his invention, **so as to cut off all question of the defeat of his patent by a use or sale of it by others more than two years prior to his application**, and thus leave open only the question of priority of invention. The evident intention of congress was to take away the right which existed under the act of 1836 to obtain a patent after **an invention had** for a long period of time **been in public use, without the consent or allowance of the inventor**; it limited that period to two years, **whether the inventor had or had not consented to or allowed the public use.**" (Emphasis added)

From this quote from *Andrews v. Hovey*, it is evident that the use or sale by others prior to filing a patent application by the inventor does not cut off the inventor's right to obtain a patent so long as the inventor files the application within the statutory period which was 2 years at the time of the *Andrews v. Hovey* decision and is now 1 year under 35 USC 102(b). (Applicants note that the U.S. Supreme Court cited *Andrew Hovey* with approval in *Pfaff v. Wells*.) Thus Prof. Tanaka's reproducing of Applicants' results reported in Applicants' article and the reporting of this in *Asahi Shinbun* article does "not cut off [Applicants'] right to obtain a patent" since Applicants have filed the present application within one year of the date of publication of Applicants' article. Applicants note that the Supreme Court says that "the consent or allowance of the inventor" is not a factor in determining whether "a use" by another cuts off the one year period under §102(b).

The Patent Office Board of Appeals in *Ex parte Powell and Davies*, 37 USPQ 285 states in regard to the publication of applicant's foreign patent application before

the filing of a U.S. application on October 5, 1936 on an invention described in the foreign patent application that:

The Examiner has also rejected the claims on the printed specification of Applicants' own British application which appears from this record to have been published on August 27, 1936. We know of no authority for such a rejection. Neither section 3886 nor section 4887 R.S. warrants the rejection. Obviously, the publication could not have a date prior to Applicants' invention. **There is no statute that requires an Applicant to make his invention in this country.**

Therefore, Applicants of the present invention can rely on their publication in Zeitschrift for Physik as evidence of their invention. Applicants note that the Board states that the statute does not require Applicants to make the invention in this country to get the benefit of the one year period under 35 USC §102(b). Therefore, the date of Applicants' invention is as least as early as the date of Applicants' publication which is before the date of the Asahi Shinbum article.

The Patent Office Board of Appeals in Ex parte Powell and Davies, 37 USPQ 285, 286 further states:

The Commissioner indicates in Ex parte Grosselin that the Examiner should consider whether the German patent was derived from Applicant and was in effect nothing more than a printed publication of Grosselin's invention.

The Asahi Shinbum article states in the first paragraph:

A new ceramic with a very high  $T_c$  of 30K of the superconducting transition has been found. The possibility of high  $T_c$  - superconductivity has been reported by scientists in Switzerland this spring. The group of Prof. Shoji

TANAKA, Dept. Appl. Phys. Faculty of Engineering at the University of Tokyo confirmed in November, that this is true.

The "scientists in Switzerland" are the inventors of the above-identified application. The Asahi Shinbum article only reports the work of Applicants and that it was reproduced by Prof. Tanaka. This article is a disclosure of Applicants' "own invention" and clearly in the words of the Board in *Ex parte Powell and Davies*, "was derived from [Applicants] and [is] in effect nothing more than a printed publication of [Applicants'] own invention and cannot be used as a reference".

The Patent Office Board of Appeals in *Ex parte Lemieux* 148, 140 states that:

Finally, we believe that our holding is consistent with decisions in interference practice wherein, even though in the usual case a party may not establish a priority date of invention by reference to activity in a foreign country, yet in an originality case where a party is seeking to prove that the other party derived from him so that there is only a single original inventor, he may be permitted to prove derivation by reference to activity abroad. ... By analogy, in the present case appellant has demonstrated that he is the single original inventor, there being no adverse party.

Following this decision it is clear from the Asahi Shinbum article that Applicants are the "single original inventor" and that the Asahi Shinbum article is "derived" from Applicants and that Professor Tanaka's work reported in the Asahi Shinbum article is "derived" from Applicants.

In *In re Mathews* 161 USPQ 276 (CCPA 1969) a patent to Dewey was cited under 35 USC 102(e) against the application of Mathews. The Dewey patent disclosed but did

not claim the invention claimed in the Mathews application. The claimed invention in the Mathews application was a circuit which Dewey disclosed to comply with 35 USC 112 requirements. Mathews submitted Dewey's affidavit under 37 CFR 132 which stated that Mathews disclosed to Dewey the circuit which Dewey described but did not claim. The CCPA held that Dewey was not a reference under 35 USC 102(e) against Mathews application stating 162 USPQ 276, 278:

It necessarily follows that Dewey may not be relied upon to defeat Mathews' application since Dewey's disclosure, *in view of the facts established in the record*, is not inconsistent with the novelty of Mathews' claimed invention, That is, *on the record here*, Dewey derived his knowledge from Mathews who is "the original, first, and sole inventor."

Following In re Mathews, it is necessary follows that the Asahi Shinbum article cannot be relied upon under 35 USC 102(a) to defect the present application since the Asahi Shinbum article states that Prof. Tanaka derived his knowledge from applicants who are the original, first, and sole inventors.

In re Mathews is directed to a reference under 35 USC 102(e) and not under §102(a). But this does not matter since under §102(e) an issued patent (which corresponds to a printed publication under §102(a)) is a reference as of the filing date (which corresponds to the publication date of a printed publication under §102(a)) and not the publication date (the issue date) of the §102(e) cited patent. Also, if the patent

cited as a §102(e) reference had issued prior to the filing date of the applicant in In re Mathews, it would have been a §102(a) reference. Thus the rationale of In re Mathews should apply to a reference cited under §102(a). The Asahi Shinbum article states that Prof. Tanaka derived his knowledge from Applicants' article and that Prof. Tanaka reproduced Applicants' work reported in Applicants' article and thus Applicants are the original, first and sole inventor.

In response to applicants' comments on the cited decisions, the Examiner states, "The applicants cite four decisions which do not directly apply to the present facts."

Applicants disagree.

In regards to In re Katz the Examiner states:

(a) The In re Katz decision held that an applicant may overcome an article as 35 USC 102(a) prior art by showing that the applicant was a co-author and that the other co-authors were under the direction and control of the applicant. Here, however, the applicants were neither co-authors in the Asahi Shinbum article nor did they exercise direction and control over the work reported in that article.

Applicants disagree. The Examiner does not cite the text of In re Katz to support this interpretation of In re Katz. In fact, In re Katz does not support the Examiner's position. In In re Katz an article co-authored by the patent applicant was cited against

the applicants' patent application under 35 USC 102(a). The application was filed less than one year after the article. In determining whether the article was prior art under 35 USC 102(a), the CCPA states "[i]t may not be readily apparent from the statutory language that a printed publication can not stand as a reference under §102(a) unless it is describing the work of another." 215 USPQ 14, 17. The inventor submitted a declaration stating that he was the sole inventor of the subject matter described in the article and that the other authors were students working under his direction. The CCPA concluded that "The applicant's declaration is sufficient in this case to overcome the rejection" under 35 USC 102(a). 215 USPQ 14, 18. There is no evidence of record that the Asahi Shinbum article describes any invention other than those of Applicants. In this regard the CCPA further states:

As an initial matter, we hold that authorship of an article by itself does not raise a presumption of inventorship with respect to the subject matter disclosed in the article. Thus, co-authors may not be presumed to be coinventors merely from the fact of co-authorship. On the other hand, when the PTO is aware of a printed publication, which describes the subject matter of the claimed invention and is published before an application is filed (the only date of invention on which it must act in the absence of other proof), the article may or may not raise a substantial question whether the applicant is the inventor. **For example, if the author (whether he is the applicant or not) specifically states that he is describing the work of the applicant, no question at all is raised.** The content and nature of the printed publication, as well as the circumstances surrounding its publication, not merely its authorship, must be considered. (Emphasis added).

It is clear from this passage that where the authors of an article are not the inventors of an invention described therein, the article is not necessarily a 102(a) reference. The above passage states "if the author (whether he is the applicant or not) specifically states that he is describing the work of applicants, no question at all is raised", that the article is not a reference under § 102(a). The Asahi Shinbum article clearly states that Prof. Tanaka reproduced applicants work reported in Applicants' article. There can be no question that the Asahi Shinbum article is not a reference under § 102(a). Moreover, "the content and nature" of the Asahi Shinbum article "as well as the circumstances surrounding the publication" clearly show that it is describing Prof. Tanaka's reproduction of Applicants' work. A published article is an invitation to all readers to reproduce and verify the work reported. Thus the Asahi Shinbum article describes no invention other than that of Applicants.

In regards to *Andrews v. Hovey* the Examiner states:

(b) The *Andrews v. Hovey* decision involved a grace period which is now codified in 35 USC 102(b). The present case involves a printed publication as prior art under 35 USC 102(a).

The Examiner's comments miss the point of *Andrews v. Hovey*. As stated above, this case clearly says that "the use" by others prior to filing of the patent application by the inventors (which would be a §102(a) reference) does not cut off the right of the inventors to obtain a patent on the application filed within the statutory period under

§102(b) from the inventors own printed publication. The Asahi Shinbum article describes "the use" of Applicants' invention by Prof. Tanaka. If such a use in the United States would not be prior art under §102(a), it is not possible for a printed publication describing such a use in a foreign country to be prior art under §102(a).

In regard to Ex parte Powell and Davies:

(c) The Ex parte Powell and Davies" decision held that an applicant's own foreign patent which issued within the grace period cannot be used against him or her.

The Examiner's comments miss the point of Ex parte Powell and Davies which explicitly states that "[t]here is no statute that requires an Applicant to make his invention in this country". Applicants initially made there invention in Zurich, before the date of the Asahi Shinbum article. Their results were published prior to the Asahi Shinbum article in Applicants' article which was in possession of the assignee of the present invention in the US prior to the date of the Asahi Shinbum article. Also, in Ex parte Powel and Davies the Applicant's British application was published before their application was filed in the United States and it was still not a valid §102(a) reference.

In regard to Ex parte Lemieux, the Examiner states

The Ex parte Lemieux" decision applied that reasoning to an applicant's own article published in another country. Again, the present applicants had no part in the writing of the Asahi Shinbum article.



Again the Examiner's comments miss the point of Ex parte Lemieux which states "in an originality case where a party is seeking to prove that the other party derived from him so that there is only a single original inventor, he may be permitted to prove derivation by reference to activity abroad". Here the Asahi Shinbum article says that Prof. Tanaka derived his work from the work of Applicants and thus the Asahi Shinbum article is not a reference against the present application.

In regard to In re Mathews the Examiner states:

"In re Mathews, 161 USPQ 276, 277-279 (CCPA 1969), held that an applicant may overcome a patent as prior art under 35 USC 102(e) with evidence that the applicant provided the knowledge for the disclosure in that patent. By contrast, the present facts involve prior art under 35 USC 102(a) with a publication date before the invention was in this country."

In the present Application the Asahi Shinbum article acknowledges that Applicants provided the knowledge to Prof. Tanaka to reproduce Applicants work which is described in Applicants' article. And since the Asahi Shinbum article refers to Applicants' discovery, as stated above, for this purpose a §102(a) reference is equivalent to a 102(e) reference.

The Examiner further states:

(3) The present facts may raise a novel issue of law." The applicants were the first to develop the presently claimed invention, but the earliest

date they can show that invention in this country is December of 1986." The Asahi Shinbum article was published in November of 1986 and describes the development of superconductivity with an oxide of La, Ba, and Cu having a perovskite structure by a third party, but that article apparently indicates that the third party was confirming the discovery of the present applicants. Notwithstanding the possible uniqueness of the present facts, however, the Asahi Shinbum article still is deemed to be prior art under 35 USC 102(a), which the applicants have not been able to overcome with a showing of an earlier date in this country or a showing of their direction and control over the work done by that third party.

35 USC §102(a) and the cited case do not require work at an earlier date in this country to overcome reference cited under §102(a). Also, §102(a) and the cited case law do not require a showing that the Applicants exercised direction and control over Prof. Tanaka or the author of the Asahi Shinbum article. In fact, 35 USC §102 and the cited cases require a contrary result as Applicants have shown above. Notwithstanding, Applicants have shown that their conception was in this country in ready to file form, in the possession of the assignee of the present invention, prior to the date of the Asahi Shinbum article.

Applicants have argued that if one would follow the rationale of the Examiner, that is, if an applicant publishes an article and some other third party reports that same result prior to applicant's filing of a patent application which is subsequently filed within one year of applicant's own publication, the reporting of applicant's work by the third party would be prior art against applicant's application. Such a result would

deny (the applicant) the one year grace period provided under 35 USC 102(b). The Examiner dismisses this argument saying

“applicants” argument is duly noted, but again, it is further noted that the reference is prior art under 35 USC 102(a). The reference is not just a republication of the applicants' article. Instead, the reference is the reporting of someone else's work which confirms the applicants' work. The applicants also are not able to show a priority date which pre-dates the publication of that reference”.

The Examiner is ignoring the fact that the Asahi Shinbum article and the work of Prof. Tanaka reported on therein was derived from Applicants. The cases cited above clearly state that when a third party derives their knowledge from an applicant, the third party's knowledge, for use or for publication of the information is not prior art against such an applicants' patent application.

### **Applicants Have Proven They Can Swear Behind the Reference**

Even though, as stated by the U.S. Supreme Court in Pfaff v. Wells, it is not necessary to show anything more than a conception to establish a date of invention under all sections of 35 USC 102 other than §102(g). Applicants have proven by facts that the conception of their invention was in the United States at their direction prior to the date of the Asahi Shinbum article, November 28, 1986, and applicants have proven that they were diligent from prior to the date of the Asahi Shinbum article by instructing coworkers in the United States until December 3, 1986 which is the date the Examiner

believes is the earliest date of Applicants reduction to practice in the United States. (For the reasons of record applicants believe that they have shown that their invention was reduced to practice in the United States prior to the date of the Asahi Shinbum article). The examiner has not rebutted applicants proof that applicants conception was in the United States at their direction prior to the date of the Asahi Shinbum article and the Examiner has not denied that applicants have proven that they were diligent by instructing coworkers in the United States from a time prior to the date of the Asahi Shinbum article until the date the Examiner believes is the date of Applicants' date of reduction to practice in the United States. The details of Applicants' proof are discussed at pages 22, line 8 to page 24, last line, of applicants' Substitute Amendment dated March 6, 1997. That argument is reproduced in detail below.

The Examiner's response to Applicants' proof is at page 19, paragraph d. ii of the final rejection "[t]he applicants further urge that they have shown clear diligence from before November 28, 1996 until actual reduction to practice at or around December 3, 1986. Nevertheless, the actual reduction in this country is deemed to have occurred on December 3, 1986, which is after the publication date for the reference." (As stated above the Examiner is in error that Applicants have to prove reduction to practice in this country before the date of the Asahi Shinbum article to avoid it as a §102(a) reference.)

Willson v. Sherts 81 F 2d 775, 28 USPO 379 (CCPA 1936) held (in an interference) that an inventor who conceives an invention outside of the United States

gets the benefit of the date that a third party, to whom the invention is disclosed, brings the conception into the United States (28 USPQ 379, 381) and that acts in this country done on behalf of the inventors can be used to show diligence to reduction to practice in the United States (28 USPQ 379, 383). Thus, the rejections of Applicants' claims under 35 USC 102 and 103 over the Asahi Shinbum article should be withdrawn.

It is noted that in the declaration of co-inventors J. G. Bednorz and K. A. Mueller dated March 21, 1988, mailed into the patent office on June 22, 1988 at paragraph 3, states "On approximately October 16, 1986, we gave Praveen Chaudhari ... six samples of the high temperature superconductive ceramic oxide materials that we had described in our aforementioned Z Physik B. publication. Praveen Chaudhari brought these samples back to the U.S. when he returned after visiting with us on or about October 16, 1986." This is evidence that these samples are brought into the United States on or about October 16, 1986. When these samples came into the United States, since they were inherently superconductive as claimed, the invention was essentially reduced to practice in the United States on that date. It is further noted that the Declaration of Alexis P. Malozenoff signed March 30, 1988 states at paragraph 3, "On or about November 15, 1986, Richard Greene and I traveled to Baltimore for a magnetics conference. During our travel to Baltimore, we discussed Greene's ongoing experiments in high  $T_c$  superconducting samples which he said had been received from Bednorz and Mueller." This is clear evidence that by November 15, 1986, superconducting samples fabricated by applicant's were being measured in the United States. These samples were inherently superconducting and, consequently,

established the reduction to practice in the United States as of that date. The Declaration of Cheng-Chung John Chi dated March 29, 1988 states at paragraph 2, "At a time prior to approximately the middle of November, 1986, Chang C. Tsuei told me a measurement he made on  $T_c$  superconducting material which he said were received from Georg Bednorz and K. A. Mueller, two physicists working for IBM Corporation in Zurich, Switzerland ... Chang Tsuei said that he had measured resistivity versus temperature of these samples." This is again further evidence that the Mueller Bednorz superconducting samples were in the United States prior to the middle of November 1986."

In the Affidavit of Sung Il Park, dated March 30, 1988, at paragraph 4, it is stated "the preparation in measurement of the aforementioned superconducting samples occurred at a date prior to November 15, 1986, and to the best of my recollection, occurred on or about November 9, 1986, the date when a Helium dower was pumped down preparatory to taking the actual measurement." Therefore, since measurements were taken prior to the date of publication of the Asahi Shinbum article, which was November 28, 1986 the invention was reduced to practice in the US prior to the publication date of the Asahi Shinbum article.

At page 11 of the Examiner's Action dated April 19, 1996, in the paragraph labeled i, the Examiner states "the applicants argue that Sung Il Park affidavit of March 30, 1988 states at para. 4 that measurements were taken of a superconductive sample on or before November 9, 1986, to the best of affiants recollection, or no later than

November 15, 1986. The document evidence is not deemed to support that argument, however." In the paragraph marked (1) on page 11 of PA, the Examiner states "plots of those measurements are missing. See the Cheng C. Tseui affidavit of March 30, 1998, para. 6." This statement comes directly out of Cheng Tseui's Declaration.

Notwithstanding, Cheng Tseui's Declaration says the measurements were made, that the plots that were taken were missing. The last sentence of this paragraph states "I believe that they may have been inadvertently thrown away when the laboratory was subsequently extensively cleaned." The Examiner further states "a hand-drawn diagram with the indication of a vacuum pumped down on November 8, 1988 also is not deemed to show that the measurements were taken." The Examiner is referring to paragraph 5 of the Cheng Tseui Declaration and Exhibit C which contains the hand-drawn figure.

At paragraph (2) of page 11 of the Examiner's Action dated April 19, 1996, the Examiner points to cablegrams sent by Dr. Greene to applicants in Zurich which are attached as Exhibit B to his Declaration. The Examiner states "Dr. Greene reports that no indication of superconductivity has been seen in his specific heat measurements for temperature 4-35°K." The Examiner fails to note that in the same cablegram dated November 11, 1986, Dr. Greene states "this is not really too surprising given the very broad transition to have found in resistivity and susceptibility." The Examiner acknowledges that "Exhibit C has pages dated December 1, 1986 on in Exhibit D, which actually has plots and resistance versus temperature dated as early as December 3, 1986." The Examiner is conceding that high  $T_c$  superconductivity was

measured on the samples which the very same set of cablegrams and affidavit say were in the United States in the middle of November 1986. Consequently, by Examiner's own admission, samples which were in the United States were clearly shown to be superconducting as of December 3, 1986. Consequently, the samples that were in the United States as of November 9 were inherently superconducting. It is clear from the same declarations that Applicants' were communicating with Dr. Greene. It is noted that Dr. Greene's cablegram dated November 25, 1986 to applicants states he will resume work on the new superconductor and that not much will happen because of the Thanksgiving Holiday until the following week. There are cablegrams dated November 26, December 1, December 2, 1986 related to high  $T_c$  superconductivity. Dr. Greene's Exhibit C has notebook pages dated December 1, 1986 to December 5, 1986. The December 5, 1986 shows  $T_c$  of 26°K and 30°K. Exhibit D show a plot of R vs. T dated December 8, 1986. Clear reduction to practice is shown and clear diligence is shown from prior to the date of the Asahi Shinbum article. This was clearly done in close correspondence with the applicants. Thus, the facts clearly shown applicant's can swear behind the Asahi Shinbum reference.

The Examiner repeats the same arguments in the final rejection without rebutting Applicants' arguments and proof that their conception was in this country at their direction and that their co-inventors in this country under their direction diligently pursued a reduction to practice in this country the earliest date of which according to the Examiner is December 3, 1986.



**Applicants Invention Was Reduced To Practice In the US Before  
The Asahi Shinbum Article**

Attachment C of this Brief is a copy of a letter from C. W. Chu to Applicants dated December 3, 1986. This letter states:

This is just to inform you that my group at the U. of Huston has reproduced your results (Z. Phys. B 64, 189 (86)) three weeks ago. ... I believe it is superconductivity.

A journal article is an invitation to any one to reproduce the work reported therein . Thus a reader of the article is for that purpose under the direction and control of the author. Thus Applicants invention was reduced to practice in this country prior to the date of the Asahi Shinbum article at the direction and control of Applicants.

The Examiner in the final rejection repeats the earlier rejection stating:

i. The applicants argue that the Sung 11 Park Affidavit of March 30, 1988 states at para. 4 that measurements were taken of a superconductive sample on or before November 9, 1986, to the best of the affiant's recollection, or no later than November 15, 1986. The documentary evidence is not deemed to support that argument, however. See MPEP 715.07.

(1) Plots of those measurements are missing. See the Chang C. Tsuei Affidavit of March 30, 1988, para. 6. A hand-drawn diagram with the

indication of vacuum pumping on November 9, 1988 also is not deemed to show that the measurements were taken.

(2) Moreover, the other evidence in the record appears to show that high temperature superconductivity was not attained in this country as of November 9 or 15, 1986. The March 30, 1986 Declaration of Richard L. Greene includes a series of cablegrams sent by Dr. Greene to the applicants in Zurich, Switzerland as Exhibit B. On both November 11, 1986 and November 14, 1986, Dr. Greene reports that no indication of superconductivity has been seen in his specific heat measurements for temperatures of 4-35°K. Exhibit C has pages dated December 1, 1986 on, and Exhibit D, which actually has plots of resistance vs. temperature, has an earliest date of December 3, 1986.

i. The applicants argue that "Praveen Chaudhari brought these samples back to the U.S. when he returned after visiting (the inventors) on or about October 16, 1986. When these samples came into the United States since they were inherently superconductive as claimed, the invention was essentially reduced to practice in the United States on that date." As stated before repeated above, however, the applicants were unable to show the attainment of superconductivity any earlier than December 3, 1986 in this country. Again, the present invention is directed to the method of superconducting electricity. That method apparently was not reduced to practice before December 3, 1986.

ii. The applicants further urge that they have shown clear diligence from before November 28, 1986 until actual reduction at or around December 3, 1986. Nevertheless, the actual reduction in this country is deemed to have occurred on December 3, 1986, which is after the publication date for the reference.

iii. The applicants assert that they should be entitled to a one-year grace period for their own published invention, but this prior art rejection is based on 35 USC 102(a) because the author of that reference is a different inventive entity.

19 The applicants' proposed priority date for the EPO application is January 23, 1987, which is after the December 1986 dates show by the Richard L. Greene Affidavit.

In these repeated rejections the Examiner has not responded to Applicants' arguments and thus has not rebutted any of them. Therefore, the Examiner concedes that Applicants' conception was in this country at their direction prior to the date of the Asahi Shinbum article and that coworkers in this country at Applicants' direction diligently reduced their invention to practice in the United States. Applicants petitioned for withdrawal of the final rejection requesting the reasons for why the 1.132 affidavits submitted did not effectively swear behind the Asahi Shinbum article. The petition was denied by the Director of Group 1700 without rebutting applicants proof of conception and diligence. Therefore, the Director of Group 1700 concedes that Applicants' conception was in this country at their direction prior to the date of the Asahi Shinbum article and that coworkers in this country at Applicants' direction diligently reduced their invention to practice in the United States. This necessarily requires a finding that the Asahi Shinbum article is not a valid §102 reference.

Therefore, the Board is respectfully requested to reverse the rejection of claims 24-26, 86-90, 96-135 and 137-177 under 35 USC § 102(a) as anticipated by Asahi Shinbum article.

## CLAIM REJECTIONS - 35 USC § 103

Claims 24-26, 86-90, 96-135 and 137-177 have been rejected under 35 U.S.C. § 103(a) as being unpatentable over Asahi Shinbum article.

Claim 136 has been allowed over the Asahi Shinbum article since according to the Examiner the examples in the present specification are deemed to show criticality for the formula of claim 136.

Since the present application was filed within one year of Applicants' article, Applicants' article is not a reference as to them (even though it would be a reference as to a third party). Thus the only portion of the Asahi Shinbum article relevant to Applicants' claims is:

A new ceramic with a very high  $T_c$  of 30K of the superconducting transition ... is an oxide compound of La and Cu with Barium which has a structure of the so-called perovskite and shows metal-like properties.

Since the Asahi Shinbum article refers to " $T_c$  of 30K" and since each of Applicants claims recites  $T_c > 26^\circ\text{K}$ , the Asahi Shinbum article alone cannot anticipate  $T_c > 26^\circ\text{K}$  since to be an anticipation a reference must contain all the limitations of the claim it is said to anticipate. Also, the Asahi Shinbum article provides no teaching of how to make the "new ceramic". A reference which does not provide a method of making a composition cannot anticipate a claim to the composition and thus to a use of that new composition. Also, the Asahi Shinbum article has no specific embodiment of the new composition. Thus it cannot anticipate under 35 USC 102. If as to Applicants the Asahi Shinbum article is not a valid §102 reference, the Asahi Shinbum article cannot render Applicants' claims obvious since to do so would render the Asahi Shinbum article a valid §102 against Applicants.

As state above the examiner's characterization of the Asahi Shinbum article does not accurately represent the teaching of this article.

Applicants' article which is incorporated in applicants' specification and priority document is directed to a Ba-La-Cu-O system. Applicants' article was submitted for publication on April 17, 1986 to Z. Phys. B from the IBM Zurich Research Laboratory in Switzerland. Thus the only teaching in the Asahi Shinbum article relevant to Applicants' claimed invention is the teaching in Applicants' article which is incorporated by reference in the present application and referred to in the priority document. The Asahi Shinbum article provides no teaching relevant to applicants' claimed invention other than the teaching in Applicants' article on how to make the ceramic "newly discovered" by applicants. The Asahi Shinbum article states the Applicants' "newly discovered" ceramic "is an oxide compound of La and Cu with Barium which has a structure of the so-called perovskite and shows metal-like properties". This is described in detail in Applicant's article. Thus the examiner is stating that it is obvious to a person of skill in the art to practice the invention of all of applicants non-allowed claims from the teaching of the Asahi Shinbum article which is the teaching of Applicants' specification which incorporates applicants' article by reference. Applicants note that they received the Nobel Prize in Physics in 1987 for their discovery reported in applicants article. Since Prof. Tanaka apparently only reproduced applicants work based on applicants' article, he did not share in the Nobel prize. Therefore, the examiner is stating that all of applicants non-allowed claims are obvious in view of applicants' teaching.

Alternatively, the examiner is stating that all of applicant's non-allowed claims are obvious in view of the Asahi Shinbum article's statement that "[a] new ceramic with a very high  $T_c$  of 30 K of the super conductive transition has been found. ... The ceramic newly discovered, is an oxide compound of La and Cu with Barium which has a structure of the so-called perovskite and shows metal-like properties. " Thus the examiner is stating that once a person of ordinary skill in the art knows that "an oxide compound of La and Cu with Barium which has a structure of the so-called perovskite and shows metal-like properties " has a "a very high  $T_c$  of 30 K" the inventions of all of applicants non-allowed claims can be made and used by such a person of ordinary skill in the art without any additional teaching other than what is known by a person of ordinary skill.

Applicants acknowledge that if a material is known to be a superconductor, a person of skill in the art would know to cool the material to below the  $T_c$  and to flow a superconducting current therein at that temperature. Prior to the date of Applicants' invention, which is at least as early as the date on which Applicants' article was published by Z. Phys. B no one knew that transition metal oxides had a  $T_c > 26$  K except for Applicants. As stated above the Asahi Shinbum article describes no invention other than that of Applicants and is thus not a valid reference.

Therefore, the Board is respectfully requested to reverse the rejection of claims 24-26, 86-90, 96-135 and 137-177 under 35 USC §103 as obvious over the Asahi Shinbum article.

## OBJECTION TO THE SPECIFICATION UNDER 35 USC 112

The examiner states:

5. The specification is objected to under 35 U.S.C. § 112, first paragraph, as failing to provide an enabling disclosure commensurate with the scope of the claims.

Applicants disagree. The specification incorporates by reference Applicants' article. In the rejection under 35 USC 102 and 103 over the Asahi Shinbum article, the examiner has stated that a person of skill in the art is enabled to practice the inventions of applicants' non-allowed claims by the mere statement that a Ba-La-Cu-O compound has been confirmed to be superconductive as described by Applicants in their article. The examiner's objection to the specification is inconsistent with the examiner's rejection under 35 USC 102(a) and 103(a).

The text of the Asahi Shinbum article merely states that Prof. Tanaka reproduced Applicants' work. Thus, the Examiner has stated that all of the inventions of applicants' non-allowed claims are contained within the Asahi Shinbum article and thus are fully enable by Applicants' article. The Examiner has also rejected all of applicants' non-allowed claims under 35 USC §103(a) in view of the Asahi Shinbum article. This means that nothing more is needed than what is described in Applicants' article and ordinary skill to practice all of Applicants non-allowed claims.



The examiner further states:

- a. The present specification is deemed to be enabled only for compositions comprising  $\text{Ba}_x\text{La}_{5-x}\text{CuO}_y$ .

The examiner again used the terminology “deemed” which means that it is the examiner’s “opinion”. The examiner has introduced no factual evidence to support the examiner’s “opinion” that “[t]he present specification is deemed to be enabled only for compositions comprising  $\text{Ba}_x\text{La}_{5-x}\text{CuO}_y$ .” As shown below, the specification cites a substantially large number of specific compositions, and provides sufficient teaching to enable a person of skill in the art to practice Applicants’ invention.

The examiner further states:

The art of high temperature (above 30 K) superconductors is an extremely unpredictable one. Small changes in composition can result in dramatic changes in or loss of superconducting properties. The amount and type of examples necessary to support broad claims increases as the predictability of the art decreases. Claims broad enough to cover a large number of compositions that do not exhibit the desired properties fail to satisfy the requirements of 35 USC 112. Merely reciting a desired result does not overcome this failure. In particular, the question arises: Will any layered perovskite material containing copper exhibit superconductivity? Also, does any stoichiometric combination of rare earth, an alkaline earth, and copper elements result in an oxide superconductor?

The examiner provides no factual evidence to support the statement “[t]he art of high temperature (above 30 K) superconductors is an extremely unpredictable one.” This is an opinion of the examiner. The examiner should withdraw the rejection, provide

factual evidence to support the opinion or submit an examiner's affidavit under MPEP 706.02(a) qualifying himself as an expert in the art of high T<sub>c</sub> superconductors to offer such a conclusory opinion. Applicants requested such an Examiner's affidavit. Since the Examiner has not provided such an affidavit, the Examiner's opinions should be disregarded. It is Applicants' teaching that controlling the amount of the constituents of the composition, such as oxygen content, effect the superconductive properties of the composition. It is a matter of routine experimentation to find the optimum constituents, such as oxygen content, for a particular high T<sub>c</sub> superconducting composition. Applicants do not have to provide experimental results for every composition that fall within the scope of their claims when a person of skill in the art exercising routine experimentation has a reasonable expectation of success following applicants teaching to achieve a composition through which can be flowed a superconducting current according to the teaching of Applicants' specification.

According to *In re Angstadt* 190 USPQ 214, 218 in an unpredictable art, §112 does not require disclosure of a test with every species covered by a claim. The CCPA states:

To require such a complete disclosure would apparently necessitate a patent application or applications with "thousands" of examples or the disclosure of "thousands" of catalysts along with information as to whether each exhibits catalytic behavior resulting in the production of hydroperoxides. More importantly, such a requirement would force an inventor seeking adequate patent protection to carry out a prohibitive number of actual experiments. This would tend to discourage inventors

from filing patent applications in an unpredictable area since the patent claims would have to be limited to those embodiments which are expressly disclosed. A potential infringer could readily avoid "literal" infringement of such claims by merely finding another analogous catalyst complex which could be used in "forming hydroperoxides."

The Examiner provides no evidence to support the examiner's statement that "[t]he amount and type of examples necessary to support broad claims increases as the predictability of the art decreases." The examiner has provided no evidence that the predictability of art of high  $T_c$  superconductivity is low. The Examiner's statement that "[c]laims broad enough to cover a large number of compositions that do not exhibit the desired properties fail to satisfy the requirements of 35 USC 112." implies that applicants claims "cover a large number of compositions that do not exhibit the desired properties" of high  $T_c$  superconductors. The Examiner has provided no evidence to support the examiners' implication. In fact, the claims do not cover any compositions that do not exhibit the desired properties of high  $T_c$  superconductors. Applicants claims only cover superconductors having  $T_c > 26^\circ\text{K}$  which carry a superconductive current. Applicants' claims are not composition of matter claims.

The Board's attention is directed to the following comments from the specification.

The specification states at page 1, lines 5-10, that "This invention relates to ... superconducting compositions including copper and/or transition metals."

The specification further states at page 5, lines 2-9 that:

"It is another object of the present invention to provide novel superconductive materials that are multi-valent oxides including transition metals, the compositions having a perovskite-like structure."

It is a further object of the present invention to provide novel superconductive compositions that are oxides including rare earth and/or rare earth-like atoms, together with copper or other transition metals that can exhibit mixed valent behavior."

The specification further states at page 8, lines 1-11, that "[A]n example of a superconductive composition having high  $T_c$  is the composition represented by the formula RE-TM-O, where RE is a rare earth or rare earth-like element, TM is a nonmagnetic transition metal, and O is oxygen. Examples of transition metal elements include Cu, Ni, Cr etc. In particular, transition metals that can exhibit multi-valent states are very suitable. The rare earth elements are typically elements 58-71 of the periodic table, including Ce, Nd, etc. If an alkaline earth element (AE) were also present, the composition would be represented by the general formula RE-AE-TM-O."

And at page 7, lines 14-15, the specification states that "the rare earths site can also include alkaline earth elements."

The specification further states at page 11, lines 19-24, that "An example of a superconductive compound having a layer-type structure in accordance with the present invention is an oxide of the general composition  $RE_2TMO_4$ , where RE stands for the rare earths (lanthanides) or rare earth-like elements and TM stands for a transition metal."

The composition  $RE_2TMO_4:RE$  is referred to at page 24, lines 5-9;  $RE_{2-x}TM_xO_{4-y}$  is referred to at page 25, lines 19-21.

The following specific compounds are recited in the application:

$Ba_4La_{5-x}Cu_5O_{5(3-y)}$  at page 10, lines 4, 10, 14.

$La_{2-x}Ba_xCuO_{4-y}$  at page 12, line 13

$La_{2-x}Ba_xNiO_{4-y}$  at page 12, line 13

$La_{2-x}Sn_xNiO_{4-y}$  at page 12, line 17

$Ce_{2-x}Cu_xNiO_{4-y}$  at page 12, line 19

$La_2CuO_4$  at page 12, line 21

$La_2CuO_{4-y}$  with  $Sr^{2x}$ ,  $Ba^{2x}$  and  $Ca^{2x}$  substitution at page 13, line 17

$La_{2-x}Sn_xCuO_{4-y}$  at page 17, line 21

$\text{La}_{2-x}\text{Ca}_x\text{CuO}_{4-y}$  at page 17, line 21

$\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$  at page 18, line 6

$\text{La}_2\text{CuO}_4:\text{Ba}$  at page 18, line 15

$\text{La}_2\text{CuO}_4:\text{Ba}$  at page 24, line 6

$\text{Nd}_2\text{NiO}_4:\text{Sn}$  at page 24, line 9

$\text{La}_2\text{CuO}_{4-y}$  doped with  $\text{Sn}^{2x}$ ,  $\text{Ca}^{2x}$  and  $\text{Ba}^{2x}$  at page 25, lines 6-18

Other compounds are given in the articles to B. Raveau, in Mat. Res. Bull., Vol. 20 (1985) pp. 667-671, and to C. Michel et al. in Rev. Claim. Min. 21 (1984) 407, both of which are incorporated by reference at page 13, lines 4-5.

The Examiner cites In re Fisher, 166 USPQ 18, In re Angstadt and Griffen, 150 USPO 214, and In re Golianni, 195 USPQ 150, in support of the statement "[t]he amount and type of examples necessary to support broad claims increases as the predictability of the art decreases".

The claims under appeal In re Fisher are directed to increasing the potency of substances containing ACTH hormones for injection into human beings. In regards to the rejection for insufficient disclosure under 35 USC 112 the CCPA states that:

"the issue thus presented is whether an inventor with the first to achieve potency of greater than 1.0 for certain types of compositions, which potency was long designed because

of its beneficial effects on humans, should be allowed to dominate *all* compositions having potencies greater 1.0, thus including future compositions having potencies in excess of those obtainable from his teachings plus ordinary skill." 166 USPQ 18, 23-24 (emphasis in the original).

The CCPA goes on to say in *In re Fisher* that:

"It is apparent that such an inventor should be allowed to dominate the future patentable inventions of others where those inventions were based in some way on his teachings. Such improvements, while unobvious from his teachings, are still within his contribution, since the improvement was made possible by his work. It is equally apparent, however, that he must not be committed to achieve this dominance by claims which are insufficiently supported and hence, not in compliance with the first paragraph of 35 USC 112. That paragraph requires that the scope of the claims must bear a reasonable correlation to the scope of enablement provided by the specification to persons of ordinary skills in the art... In cases involving unpredictable factors, such as most chemical reactions... the scope of enablement obviously varies inversely with the degree of unpredictability of the factors involved." (166 USPQ 18, 24)

Applicants of the present invention have provided the first teaching that transition metal oxides can form a superconductor having a critical temperature in excess of 26°K, therefore, "is apparent that such an [applicant] should be allowed to dominate the future patentable inventions of others when those inventions [are based in some way on applicants] teaching" as stated by the CCPA in *In re Fisher Supra*.

In the present invention Applicants are acknowledged to be the pioneers of high  $T_c$  superconducting metal oxides. The Examiner has produced no evidence that invention which come within the scope of Applicants' claim cannot be achieved by persons of skill in the art based on Applicants teaching. The affidavits of Mitzi, Dinger, Tsuei, Shaw and Duncombe and the book of Poole et al. state it is straight forward to use the general principles of ceramic science to make high  $T_c$  transition metal oxide superconductors following Applicants teaching.

The claimed invention in *re Angstadt and Griffen* (190 USPQ 214) involves a methods of catalyically oxidizing alkylaromatic hydrocarbons to form a reaction comprising the corresponding hydroperoxides. The method employs catalysts. The Examiner rejected all the claims under 35 USC 112, first and second paragraphs. The Board's rational for affirming the Examiner's rejection was directed primarily to the enablement required of the first paragraph.



The CCPA reversing stated that:

"what is a maximum concern in the analysis of whether a particular claim is supported by the disclosure in an application, is whether the disclosure contains sufficient teaching regarding the subject matter of the claims as enabled one of skill in the art to make and to use the claimed invention. These two requirements 'how to make' and 'how to use' have some times been referred to in combination as the 'enablement requirement'... The relevancy may be summed up as being whether the scope of enablement provided to one of ordinary skill in the art by the disclosure as such as to be commensurate with the scope or protection sought by the claims. (190 USPQ 214,47 citing In re Moore 169 USPQ).

In the attached affidavits under 37 CFR 132, Dr. T. Dinger, Dr. Tsuei, Dr. Shaw, Mr. Duncombe and Dr. D. Mitzi state:

"That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication, can make the transition metal oxide compositions encompassed by claims 24-26, 86-90 and

96-108, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the work of Bednorz and Müller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery."

In the paragraph at the bottom of page 15 of the specification, it is stated that: in regard to compositions according to the present invention that "their manufacture generally follows the known principles of ceramic fabrication." Thereafter, an example of a typical manufacturing process is given.

The CCPA in *In re Angstadt and Griffen* further states that:

"we cannot agree with the Board that Appellants' disclosure is not sufficient to enable one of ordinary skill in the art to practice the invention without undue experimentation. We note that many chemical processes and catalytic processes particularly, are unpredictable, ... , and the scope of enablement varies inversely with the degree of unpredictability involved... The question, then, whether in an unpredictable art, section 112 requires the disclosure of a test with every species covered by a claim. To require such a complete disclosure will apparently necessitate a patent application or applications with 'thousands ' of examples... . More

importantly, such a requirement would force an inventor to seek adequate patent protection to carry out a prohibited number of natural experiments. This would tend to discourage inventors in filing patent applications in an unpredictable area since the patent claim would have to be limited those embodiments which are expressly disclosed. A potential infringer could readily avoid 'infringement of such claims' by merely finding another analogous (example) which could be used..." 190 USPQ 124, 218.

The CCPA in *In re Angstadt* further goes on to say

"having decided that appellants are *not* required to disclose every *species* encompassed by the claims even in an unpredictable art such as the present record presents, each case must be determined on its own facts." 190 USPQ 214, 218. (emphasis in the original).

In regards to the catalyst *In re Angstadt* and *Griffen* CCPA further states:

"since appellants have supplied the list of catalysts and have taught how to make or how to use them, we believe that the experimentation required to determine which catalyst will produce hydroperoxide would not be undue and certainly would not 'require ingenuity beyond that to be expected of one of ordinary skill in the art'. 190 USPQ, 214, 218 in *re Field v. Conover* 170 USPQ, 276, 279 (1971).

As stated in the affidavits of Dr. Dinger, Dr. Tsuei, Dr. Shaw, Mr. Duncombe and Dr. Mitzi, to make the high temperature superconductors encompassed by Applicants' claims, using the teaching of the present invention would not require ingenuity beyond that expected of one of ordinary skill in the art.

The CCPA in *In re Angstadt* further states that:

"the basic policy of the Patent Act, which is to encourage disclosure of inventions and thereby to promote progress in the useful arts. To require disclosures in patent applications to transcend the level of knowledge of those skilled in the art would stifle the disclosure of inventions in fields man understands imperfectly." 190 USPQ 214, 219.

The CCPA further states that:

"the certainty which the law requires in patents is not greater than is reasonable." 242 USPQ, 270-271, cited in *In re Angstadt*. 190 USPQ 214, 219.

*In re Angstadt* further states at 190 USPQ 219:

We note that the PTO has the burden of giving reasons, supported by the record as a whole, why the specification is not enabling. *In re*

Armbruster, 512 F.2d 676, 185 USPQ 152 (CCPA 1975). Showing that the disclosure entails undue experimentation is part of the PTO's initial burden under Armbruster; this court has never held that evidence is necessary for any experimentation, however slight, is sufficient to require the applicant to prove that the type and amount of experimentation needed is not undue.

By calling the claimed "invention" the "scope of protection sought" the dissent obscures the problem and frustrates the intended operation of the patent system. Depriving inventors of claims which adequately protect them and limiting them to claims which practically invite appropriation of the invention which avoiding infringement inevitably has the effect of suppressing disclosure. What the dissent seem to be obsessed with is the thought of catalysts which won't work to produce the intended result. Applicants have enabled those in the art to see that this is a real possibility, which is commendable frankness in a disclosure. Without undue experimentation or effort or expense the combinations which do not work will readily be discovered and, of course, nobody will use them and the claims do not cover them. The dissent wants appellants to make everything predictable in advance, which is impracticable and unreasonable.

We hold that the evidence as a whole, including the inoperative as well as the operative examples, negates the PTO position that persons of ordinary skill in this art, given its unpredictability, must engage in undue experimentation to determine which complexes work. The key word is "undue," not "experimentation."

The only facts which the Examiner offers as evidence of unpredictability are examples provided in Applicants' specification. The CCPA in *In re Angstadt* says that

this is "commendable frankness" which is not to be held against Applicants. The Examiner has provided no evidence that a person of skill in the art has to engage in undue experimentation to practice Applicants non-allowed claims. The affidavits of Mitzi, Dinger, Tsuei, Shaw and Duncombe and the book of Poole et al. indicate that persons of skill in the art do not have to engage in undue experimentation to practice Applicants' invention.

The Examiner cited In re Colianni 195 USPQ 150 which applicants believe is not on point since in In re Colianni "[t]here is not a single specific example or embodiment by way of an illustration of how the claimed method is to be practiced." (195 USPQ 150, 152). In contradistinction as noted above, there are numerous examples cited in applicants' specification and incorporated references. Thus this decision is not on point.

"Showing that the disclosure entails undue experimentation is part of the PTO's initial burden." In re Armbruster 185 USPQ 152, 504.

"The practical approach followed consistently by [the CCPA] ..., places the initial burden on the PTO to show that the enabling disclosure is not commensurate in scope with the claim. Upon such a showing, the burden of rebuttal shifts to applicants". In re Coliani 195 USPQ 150.

"However, [the CCPA] has made it clear that the Patent and Trademark Office must substantiate its rejections for lack of enablement with reasons" In re Armbruster 185 USPQ 152, 153.

The Examiner has merely asserted without support that "the art of high temperature superconductivity is unpredictable...".

The CCPA in In re Marzocchi, 58 CCPA 1069, 439 F. 2d 220, 169 USPQ 367, 369-370 (1971) states:

"The only relevant concern of the Patent Office under these circumstances should be over the *truth* of any such assertion. The first paragraph of §112 requires nothing more than objective enablement. How such a teaching is set forth, either by the use of illustrative examples or by broad terminology, is of no importance.

As a matter of Patent Office practice, then, a specification disclosure which contains a teaching of the manner and process of making and using the invention in terms which correspond in scope to those used in describing and defining the subject matter sought to be patented *must* be taken as in compliance with the enabling requirement of the first paragraph of §112 *unless* there is reason to doubt the objective truth of the statements contained therein which must be relied on for enabling

support. Assuming that sufficient reason for such doubt does exist, a rejection for failure to teach how to make and/or use will be proper on that basis; such a rejection can be overcome by suitable proofs indicating that the teaching contained in the specification is truly enabling...

[I]t is incumbent upon the Patent Office, whenever a rejection on this basis is made, to explain *why* it doubts the truth or accuracy of any statement in a supporting disclosure and to back up assertions of its own with acceptable evidence or reasoning which is inconsistent with the contested statement. Otherwise, there would be no need for the applicant to go to the trouble and expense of supporting his presumptively accurate disclosure. [Emphasis in original footnote deleted].

Applicants have submitted herewith affidavits of Dr. Mitzi, Dr. Tsuei, Dr. Shaw, Mr. Duncombe and Dr. Dinger under 37 CFR 132 which state, as quoted above, that once a person of skill in the art knows of applicants' work, the compositions encompassed by the claims under experimentation, can be made using the teaching of applicants without undue experimentation.

Thereby rebutting the Examiner's statement that:

"[the specification ... [fails] to provide an enabling disclosure commensurate with the scope of the claims."



The Examiner cites *In re Cooks and Cosden Oil v. American Hoechst* to support the statement “[c]laims broad enough to cover a large number of compositions that do not exhibit the desired properties fail to satisfy the requirement of 35 USC 112.” Applicants claims do not read on any inoperative specifics since Applicants' claims are method of use claims. A composition which does not have a  $T_c > 26^\circ\text{K}$  is not within the scope of the claims. Thus these decisions are not on point.

The Examiner cites *In re Corkill* as support for this statement “[m]erely reciting a desired result does not overcome this failure”. The CAFC held “[c]laims which include a substantial measure of inoperatives ... are fairly rejected under 35 USC 112.” Applicants' claims include no inoperatives. Since Applicants claims are method of use claims they are functional and thus exclude inoperatives. “[T]he use of functional language is sanctioned specifically by ... section 112.” *In re Angstadt* 190 USPQ 214, 217.

The Examiner cited *Brenner v. Manson* for the statement “a patent is not a hunting license. It is not a reward for the search, but a reward for its successful conclusion.” The claim in question was a method of making a composition. The composition had no known use. The method was found to lack utility and thus is not be patentable. This is not relevant to §112, first paragraph. Thus this decision is not on point. Moreover, Applicants have had a successful conclusion, they won a Nobel Prize and initiated and enabled the high  $T_c$  transition metal oxide art.

The Examiner queries "[w]ill any layered perovskite material containing copper exhibit superconductivity?" and "does any stoichiometric combination of rare earth, an alkaline earth, and copper elements result in an oxide superconductor?" Since applicants claims are directed to methods of using oxide compositions, applicants' claims read on only those layered perovskite materials which exhibit superconductivity with a  $T_c > 26^\circ\text{K}$  and do not read on methods of use of oxide compositions which are not superconductive. Thus the Examiner's queries is not relevant to applicants claims. Applicants are not claiming a composition which is a high  $T_c$  superconductor. Thus applicants claims do not read on any layer perovskite, or any other stoichiometric combination, but only those carrying a high  $T_c$  superconducting current. Method of use claims are inherently narrower in scope than composition claims.

The paragraph bridging pages 13 and 14 refer to Ba-La-Cu-O systems having different crystallographic phases having  $\text{Cu}^{3+}$  and  $\text{Cu}^{2+}$  ions or  $\text{Ni}^{3+}$  and  $\text{Ni}^{2+}$  ions.

Claim 103 of the present invention recites "a copper oxide compound having a layer-type-perovskite-like crystal structure, the copper oxide compound including at least one rare-earth or rare-earth-like element, and at least one alkaline-earth element". In regard to the stated elements, the rare earth elements are defined in the specification at page 7, lines 9-12 to be "a group IIIB element, such as La." Group IIIB includes Sc, Y, La and Ac, rare earth-like or near rare earth. The rare earth elements are elements 58 to 71. This group contains four elements from group IIIB and fourteen

elements from the rare-earth for a total of 18 elements. The alkaline earths contain the elements of Group A which has 6 elements.

The Examiner further states:

It should be noted that at the time the invention was made, the theoretical mechanism of superconductivity in these materials was not well understood. That mechanism still is not understood. Accordingly, there appears to be little factual or theoretical basis for extending the scope of the claims much beyond the proportions and materials actually demonstrated to exhibit high temperature superconductivity. A "patent is not a hunting license. It is not a reward for the search, but a reward for its successful conclusion".'

The Examiner has provided no evidence to support the statement "that at the time the invention was made, the theoretical mechanism of superconductivity in these materials was not well understood. That mechanism is still not understood." Applicants request the Examiner to introduce evidence to support this statement or to place an Examiner's affidavit under MPEP 706.02(a) qualifying the Examiner as an expert to make this statement. The Examiner further states "there appears to be little factual or theoretical basis for extending the scope of the claims much beyond the proportions and materials actually demonstrated to exhibit high temperature superconductivity." This is the Examiner's unsupported opinion. The five affidavits of Mitzi, Dinger, Tsuei,

Shaw and Duncombe under 37 CFR 1.132 and the book to Poole et al. described below provide factual evidence supporting Applicants position that once a person of skill in the art knew from Applicant's article that transition metal oxides were high Tc superconductors, it was a matter of routine application of the general principles of ceramic science to fabricate transition metal oxide superconductors other than those actually made by applicants. Quoting "Brenner v. Manson", 283 US 518, 148 USPQ 689, the Examiner further states that a "patent is not a hunting license. It is not a reward for the search, but a reward for its successful conclusion." The evidence introduced by Applicants clearly shows that Applicant's article upon which the present application is based had a very successful conclusion. Applicants started the field of high Tc superconductivity. All the further developments were based on Applicants teaching. Moreover, the issue in Brenner v. Manson was the patentability of a method to fabricate a composition. The composition had no use. The method was found not patentable for lack of utility. To issue a patent for such a process would be granting a hunting license for a utility that may occur in the future. This case has nothing to do with §112 enablement.

In view of the above Applicants request the Board to reverse the Examiner's objection to the specification.

## **CLAIM REJECTIONS UNDER 35 USC §112, FIRST PARAGRAPH**

Claims 24-26, 86-90, 96-113, 129-131, 134, 135, and 139-177 are rejected under 35 U.S.C. § 112, first paragraph, for the same reasons set forth by the Examiner in the objection to the specification. Applicants disagree for the same reasons why Applicants disagreed to the objection to the specification above. The Examiner provides specific comments only in regards to claims 24, 86, 88, 96 and 103.

Applicants disagree with the Examiner's statement that Applicants' arguments filed April 11, 1996, January 3, 1996, and September 29, 1995, paper nos. 53, 50, and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996, paper nos. 49 and 52, have been fully considered but they are not deemed to be persuasive. The arguments of those papers are incorporated herein by reference.

The Examiner further states:

"The additional case law and arguments by the applicants have been duly noted. For the reasons that follow, however, the record as a whole is deemed to support the initial determination that the originally filed disclosure would not have enabled one skilled in the art to make and use the invention to the scope that it is presently claimed."

The Examiner again uses the word "deemed", that is, it is the Examiner's opinion unsupported by any factual evidence. The quoted passage is completely contrary to the Examiner's rejection under 35 USC 102(a) and 103(a). Under these rejections the Examiner found the Asahi Shinbum article would have enabled one skilled in the art to make and use the invention to the scope that it is presently claimed. As noted above, the Asahi Shinbum article relies upon Applicants article. Applicants' view is further supported by the five affidavits of Mitzi, Tsuei, Dinger, Shaw and Duncombe under 37 CFR 1.132 and the book of Poole which will be described below and which states that once it was known from Applicants article that transition metal oxides were superconductive at temperatures above 26°K, other high T<sub>c</sub> transition metal oxides could be made by a person of skill in the art using the teaching of Applicants and the general teachings of ceramic science.

The Examiner further states:

ii. The applicants quote several passages from their specification at pp. 13-15 of their September 29, 1995 Amendment, but the issue is the scope of enablement, not support. The present disclosure may or may not provide support for particular embodiments, but the issue here is the scope to which that disclosure would have taught one skilled in the art how to make and use a composition which shows the onset of superconductivity at above 26°K.

Applicants are not required to provide experimental evidence for every species within the scope of their claims. The entire filed of high  $T_c$  superconductivity is based on Applicants' work, in particular, on Applicants' article. This affidavit of James W. Leonard under 37 CFR 1.132 submitted on December 15, 1998 states that 5,689 articles cited Applicants' article (Z. FurPhys. B, 64, pp. 185-193 (September 1986)). This is clear evidence that Applicant article originated and enabled the filed of high  $T_c$  superconductivity. It is clear by the facts presented by Applicants that they "have taught one of skill in the art how to make and use a composition which shows the onset of superconductivity at above 26°K". The Examiner has introduced no factual evidence to the contrary. The Examiner merely "deems" that Applicants' claims are not enabled.

The Examiner further states:

- iii. Construed in light of that issue, the invention is not deemed to have been fully enabled by the disclosure to the extent presently claimed.

The Examiner again "deems" Applicants claims not enabled without factual support.

The Examiner further states:

- (1) In their September 29, 1995 Amendment, the applicants argue that their disclosure refers to "the composition represented by the formula RE-TM-0, where RE is a rare earth or rare earth-like element, TM is a

nonmagnetic transition metal, and O is oxygen", and list several species such as " $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ " which they indicate are found in the present disclosure.

Applicants disagree. The passages quoted in the September 29, 1995 amendment lists numerous specific compositions and generic formula as indicated above. The listed species were preferred embodiments at the time of filing the present application. Preferred embodiments do not provide a limitation to the broad scope of applicants teaching.

The Examiner further states:

(2) Notwithstanding that argument, it still does not follow that the invention is fully enabled for the scope presently claimed. The claims include formulae which are much broader than the RE-TM-0 formula cited in the disclosure. Claim 24 recites "a transition metal oxide", claim 88 "a composition", and claim 96 "a copper-oxide compound".

As noted above the specification at page 1, line 5-10, states "[t]his invention relates to ... superconducting compositions including copper and/or transition metals." And at page 5, lines 5-9 "[i]t is [an] ... object of the present invention ... to provide novel superconductive compositions that are oxides."



The Examiner further states:

(a) The present specification actually shows that known forms of "a transition metal oxide", "a composition", and "a copper-oxide compound" do not show the onset of superconductivity at above 26°K. At p. 3, line 20, through p. 4, line 9, of their disclosure, the applicants state that the prior art includes a "Li-Ti-O system with superconducting onsets as high as 13.7°K. " Official Notice is taken of the well-known fact that Ti is a transition metal. That disclosure also refers to "a second, non-conducting CuO phase" at p. 14, line 18.

Applicants claims are directed to "transition metal oxides", "a composition" and "a copper-oxide compound" having a  $T_c$  in excess of 26°K which is carrying a superconducting current. Applicants claims do not include in the claimed method compositions having  $T_c < 26^\circ\text{K}$ . Thus the examples on page 3, line 20 - page 4, line 9, are not included in applicants claims. That these are transition metal oxides having  $T_c < 26^\circ\text{K}$  does not mean that Applicants' claims directed to transition metal oxides, compositions and copper oxides having  $T_c > 26^\circ\text{K}$  are not enabled. Applicants provide the teaching on how to fabricate such oxides having  $T_c > 26^\circ\text{K}$ . The "second non-conducting CuO phase" referred to at page 14, line 18, again does not mean that applicants claims are not enabled. Applicants statements at page 14 is part of applicants teaching on how to achieve an oxide having a  $T_c > 26^\circ\text{K}$ . The Examiner is attempting to use Applicants complete description of their teaching to show lack of

enablement when, in fact, this complete teaching provides full enablement by showing how samples are and are not to be prepared. Applicants have claimed their invention functionally, that is, as a method of use so the Applicants' claim do not read on inoperable species. What the Examiner "seems to be obsessed with is the thought of [transition metal oxides] which won't work to produce the intended result. Applicants have enabled those of skill in the art to see that this is a real possibility which is commendable frankness in a disclosure." In re Angstadt, Supra.

The Examiner further states:

(b) Accordingly, the present disclosure is not deemed to have been fully enabling with respect to the "transition metal oxide" of claim 24, the "composition" of claim 88, or the "copper-oxide compound" of claim 96.

Again without facts the Examiner "deems" Applicants' claims not enabled and for the reasons given above applicants disagree. The only attempt at a factual support for the Examiner's statement are the examples provided by Applicants which show  $T_c < 26^\circ\text{K}$ . Applicants provide this teaching so that a person of skill in the art will be fully informed on how to practice Applicants invention.

The Examiner further states:

(3) The examples at p. 18, lines 1-20, of the present specification further substantiates the finding that the invention is not fully enabled for the scope presently claimed.

(a) With a 1:1 ratio of (Ba, La) to Cu and an x value of 0.02, the La-Ba-Cu-O form (i.e., "RE-AE-TM-0", per p. 8, line 11) shows "no superconductivity".

This part of Applicants' teaching providing a complete teaching which permits a person of skill in the art to be fully enabled to practice Applicants' claimed invention. The issue according to *In re Angstadt* (referred to above) is whether Applicants have enabled those of skill in the art to practice Applicants invention without undue experimentation. That a person of skill in the art has to do experimentation to determine suitable combinations of elements to form a composition having  $T_c > 26^\circ\text{K}$  through which a superconductive current flows is not an indication of a lack of enablement. Thus Applicants cited examples of compositions having  $T_c < 26^\circ\text{K}$  does not show lack of enablement.

The Examiner further states in regards to the examples at p. 18, lines 1-20:

(b) With a 2:1 ratio of (Ba, La) to Cu and an x value of 0.15, the La-Ba-Cu-O form shows an onset of superconductivity at " $T_c = 26^\circ\text{K}$ ". It should be noted, however, that all of the claims in this application require the critical temperature ( $T_c$ ) to be "in excess of  $26^\circ\text{K}$ " or "greater than  $26^\circ\text{K}$ ".

Applicants do not believe that an onset of a  $T_c$  at  $26^\circ\text{K}$  is different than and greater than  $26^\circ\text{K}$ . Greater than  $26^\circ\text{K}$  can mean  $T_c = 26^\circ\text{K}$  plus some infinitesimal temperature.

The Examiner further states:

(c) Consequently, the present disclosure is not deemed to adequately enable the full scope of the present claims. Independent claims 86 and 103 may require the presence of rare earth, alkaline earth, and transition metals, but the aforementioned examples show that superconductivity is still very unpredictable. Those claims cannot be deemed to be fully enabled.

The Examiner again "deems" claims 86 and 103 as not fully enabled. This again is the Examiner's opinion. Claims 86 and 103 do not read on the examples cited in

Applicants' specification which are superconductors having  $T_c < 26^\circ\text{K}$ . Thus these examples are not evidence that claims 86 and 103 are not enabled. The examples are part of the teaching enabling a person of skill in the art to practice the invention of claims 86 and 103.

The Examiner further states:

iv. The applicants also have submitted [five] affidavits attesting to the applicants' status as the discoverers of materials that superconduct  $> 26^\circ\text{K}$ . Each of the affidavits further states that "all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar manner (way)". Each of the affidavits add "(t)hat once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above  $26^\circ\text{K}$ , such a person of skill in the art, using the techniques described in the (present) application, which includes all known principles of ceramic fabrication, can make the transition metal oxide compositions encompassed by (the present) claims ... without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art."

Applicants acknowledge that all five affiants are the employees of the assignee of the present application. (The affidavit of Shaw and Duncombe were submitted after

the date of the final rejection and were considered as indicated by the Advisory Action dated February 25, 1999).

The Examiner states in response to the affidavits of Mitzi, Tsuei and Dinger:

(1) Those affidavits do not set forth particular facts to support the conclusions that all superconductors based on the applicants' work behave in the same way and that one skilled in the art can make those superconductors without undue experimentation. Conclusory statements in an affidavit or specification do not provide the factual evidence needed for patentability.

The Examiner cited *In re Lindner*, 173 USPQ 356, 358 (CCPA 1972) in support of this statement. In *In re Lindner* the patent applicant submitted Rule 132 affidavit based on one example to show unexpected results for a claim of broader scope. The CCPA held that "[i]t is well established that objective evidence of non-obviousness must be commensurate in scope with the claims." *In re Lindner* is not on point since it does not deal with the issue of enablement. A single example can enable a broader scope claim where nothing more is needed than what is taught by Applicants or what is taught by Applicants together with what is known by a person of skill in the art.

The affidavits of Mitzi, Tsuei, Dinger, Shaw and Duncombe are statements of experts in the ceramic arts. The Examiner disagrees with these experts. But the

Examiner has not submitted an Examiner's affidavit qualifying himself as an expert to rebut the statements of Applicants affidavits.

The Examiner further states:

(2) Those affidavits do not overcome the non-enablement rejection.

The present specification discloses on its face that only certain oxide compositions of rare earth, alkaline earth, and transition metals made according to certain steps will superconduct at  $>26^{\circ}\text{K}$ .

Applicants disagree. The affidavits of Shaw and Duncombe cites numerous books and articles which provide the general teaching of ceramic science at the time of and prior to the filing date of the present application. The affidavit of Duncombe also provides several hundred pages copied from Mr. Duncombe's notebooks starting from before Applicants' filing date. In regards to these pages, Mr. Duncombe states "I have recorded research notes relating to superconductor oxide (perovskite) compounds in technical notebook IV with entries from November 12, 1987 to June 14, 1998 and in technical notebook V with entries continuing from June 7, 1988 to May 1989." Mr. Duncombe's affidavit list some of the compounds prepared using the general principles of ceramic science:  $\text{Y}_1 \text{Ba}_2 \text{Cu}_3 \text{O}_x$ ,

$\text{Y}_1 \text{Ba}_2 \text{Cu}_3 \text{O}_3$ ,  $\text{Bi}_{2.15} \text{Sr}_{1.98} \text{Ca}_{1.7} \text{Cu}_2 \text{O}_{8+8}$ ,  $\text{Ca}_{(2-x)} \text{Sr}_x \text{Cu O}_x$  and  $\text{Bi}_2 \text{Sr}_2 \text{Cu O}_x$ .

The Examiner further states:

(3) Those affidavits are not deemed to shed light on the state of the art and enablement at the time the invention was made. One may know now of a material that superconducts at more than 26 °K, but the affidavits do not establish the existence of that knowledge on the filing date for the present application. Even if the present application "includes all known principles of ceramic fabrication", those affidavits do not establish the level of skill in the ceramic art as of the filing date of that application.

The Examiner states that "these affidavits are not **deemed** to shed light on the state of the art and enablement at the time the invention was made," that is, it is the Examiner's opinion. Applicants disagree. The affidavits clearly state that all that is needed is Applicants' teaching and the ordinary skill of the art to practice applicants claimed invention. Also, 35 USC §112, does not require that enablement be determined "at the time the invention was made". This language appears in 35 USC §103, but not in 35 USC §112. Thus it is clear that it was not the intent of Congress to determine enablement at the time the invention was made in the manner suggested by the Examiner. All that is necessary is "[t]he specification shall contain a written description ... to enable any person skilled in the art ... to make and use the same." Applicants initiated the filed of high  $T_c$  superconductors. If a person of skill in the art from the description in Applicants' specification can practice applicants' claimed invention, it is enabled. Applicants' are not required to show that a person of skill in the



art had the knowledge prior to Applicants' invention. If this were the case Applicants would not be the first, sole and only inventors, since the invention would be known by others. Applicants teach ceramic processing methods to fabricate high  $T_c$  superconductors. This uses general principles of ceramic science known prior to the filing date of the present application. Thus applicants' claims are fully enabled. The Examiner has provided no evidence to the contrary. The Examiner has produced no evidence to demonstrate that a person of skill in the art, at the time of applicants filing date, could not practice the claimed invention from Applicants teaching. The utilization of such teaching to practice Applicants' claimed invention was not known prior to Applicants' filing date. That is Applicants' discovery and thus why they are entitled to their claimed invention.

The Examiner further states:

(4) It is fully understood that the applicants are the pioneers in high temperature metal oxide superconductivity. The finding remains, nonetheless, that the disclosure, is not fully enabling for the scope of the present claims.

If Applicants pioneered the field of high  $T_c$  superconductivity, that is, they initiated the substantial worldwide effort to validate their discovery and to synthesize others specific embodiment of their generic and specific teaching, then applicant s should be entitled to generic claims since other based their work on applicants' teaching.

The Examiner has cited the following seven decisions, which have been discussed in detail above, in support for the determination of non-enablement: In re Fisher, 166 USPQ 18, 24; and In re Angstadt and Griffen, 190 USPQ 214, 218. In re Colianni, 195 USPQ 150, 153, 154 (CCPA 1977). In re Cook, 169 USPQ 298, 302; and Cosden Oil v. American Hoechst, 214 USPQ 244, 262. In re Corkill, 226 USPQ 105, 1009. Brenner v. Manson, 383 US 519, 148 USPQ 689.

The Examiner has not applied the rational of these decisions. In fact, in the prosecution Applicant pointed out that the Examiner seems to have specifically avoided applying this case law and, consequently, applicants take the Examiner's silence as concurrence in the manner that applicants have applied this case law. In response to this the Examiner states "[n]otwithstanding the applicants' commentary on caselaw, the April 15, 1997 Office Action, paper no. 54, sets forth the factual basis for the determination of non-enablement at pp. 5-10." It is applicants view that the Examiner is misapplying this case law.

In this regard the Examiner further states:

(3) The applicants still further argues "that the Examiner does not rebut the case law and argument provided by applicants on (pages) 15-25 of their September 29, 1995 amendment which addresses (these issues) in detail." The point remains, nevertheless, that there appears to be a

concurrence as to the applicable caselaw. That caselaw speaks for itself. What has been fully addressed in the previous Office Action and repeated above is the factual basis for the determination of non-enablement for the scope of the present invention.

Case law does not speak for itself. The rule of a case depends on the facts of the case. The fact circumstances in the case must be compared with those of the present application to justify application of the decision of the case. The Examiner has not done this. Applicants have shown above that the case law when properly applied support Applicants' position that their claims are enabled and does not support the Examiner's position that the non-allowed claims are not enabled.

The Examiner states:

ii. The applicants urge that "their disclosure supports a substantially broader scope than (particular) species." With respect to transition metals, the applicants point to the support in their disclosure and argue that they were enabled for transition metals other than just copper. Again, however, it is noted that high temperature superconductivity is a highly unpredictable art. In view of the record as a whole, it is again determined that one skilled in the art would not have been enabled to practice the presently disclosed invention with transition metals other than copper.

"The first paragraph of §112 requires nothing more than objective enablement , how such teaching is set forth , either by the use of illustrative examples or by broad terminology is of no importance" In re Marzochi, Supra. The Examiner has provided no factual evidence to support the Examiner's statement that the field of high  $T_c$  superconductivity is unpredictable. The Examiner has attempted to support this position based on Applicants' teaching. That teaching is part of Applicants' enabling disclosure. In the last sentence of the passage above the Examiner implies that applicants claims directed to copper are enabled. Applicants teach transition metals. Copper is a transition metal. Applicants teaching enable persons of skill in the art to make transition metal oxides which sustain a superconducting current at  $T_c > 26^\circ\text{K}$ . The Examiner has provided no factual evidence that Applicants claims are not enabled for transition metals.

The Examiner states:

iii. The applicants argue that their own examples do not support the determination of non-enabling scope of the invention. Nevertheless, the record is viewed as a whole. If the applicants could not show superconductivity with a  $T_c > 26^\circ\text{K}$  for certain compositions falling within the scope of the present claims, it is unclear how someone else skilled in the art would have been enabled to do so at the time the invention was made.

The Examiner incorrectly states "applicants could not show superconductivity with  $T_c > 26^\circ\text{K}$  for certain compositions falling within the scope of the present claims." The present claims are directed to a method of flowing a superconducting current in a composition having a  $T_c > 26^\circ\text{K}$ . If a composition has a  $T_c < 26^\circ\text{K}$ , a method of flowing a superconducting current in such a compound cannot fall within the scope of applicants claims. Applicants are not claiming a composition of matter. They are claiming their discovery, passing a superconductive current through a transition metal oxide having a  $T_c > 26^\circ\text{K}$ . No one prior to applicants knew this. That is why they received the Nobel Prize in Physics in 1987.

The Examiner further states that Applicants' affidavits are conclusory. The Examiner appears to be placing himself up as an expert in the field of superconductivity. Applicants requested that the Examiner submit an affidavit in the present application rebutting the position taken by applicants' five affiants, but the Examiner has not submitted an affidavit. The facts are that the five affiants are experts in the art, the Examiner is not. The Examiner states that those "affidavits were insufficient because they were conclusory only, i.e., they lacked particular facts to support the conclusions reached". Applicants submitted the affidavit of Peter Duncombe which has provided hundreds of pages of notebook entries showing that he fabricated superconductive transition metal oxides according to the teaching of applicants specification.

The Examiner has provided no substantial evidence to support this assertion of non-enabling scope of the invention. It is requested that the Examiner support his assertion with factual evidence and not unsupported statements.

The Examiner is applying an incorrect standard of enablement. The Examiner is applying a standard applicable to composition of matter. Applicants are not claiming a composition of matter. As shown by applicants prior comments applicants have in fact fully enabled the composition of matter. Therefore, applicants have provided excess enablement for the claimed invention. The standard of enablement for a method of use is not the same as the standard of enablement for a composition of a matter. Notwithstanding, it is well settled law that claims to a composition of matter can encompass a number of inoperable species. However, Applicants' claims do not cover any inoperable species. The claims only encompass methods of flowing a superconducting current in transition metal oxides that are superconducting at temperatures in excess of 26°K. Those transition metal oxides that are not superconducting at temperatures in excess of 26°K are not encompassed by applicants claims reciting these limitations. Applicants note that a claim to a composition of matter is dominant to any use of that composition of matter and claims directed to a method of use of a composition of matter are necessarily of narrower scope than claims to the composition of matter. Applicants' claims do not encompass uses other than those which the claims are limited to by the use limitations recited in the claims. Applicants' claims are directed to what they have discovered. Therefore, applicants' claims fully satisfy the requirements of 35 USC 112.

The claimed invention is enabled because it is directed to a method of use rather than a composition. Applicants are claiming their discovery, showing superconducting current in a transition metal oxides with a  $T_c > 26^\circ\text{K}$ . If a patent applicant claims a method of flowing current through a circuit having a resistive element, the applicant does not have to describe every method of making every type of resistive element for the claim to dominate all resistive elements. Such a claim reads on resistive elements made of materials not known at the time of filing since the discovery is not the material but the method of use. Applicants discovered that a superconducting current can be flowed in a transition metal oxides having a  $T_c > 26^\circ\text{K}$ . That is what applicants are claiming.

Process of use claims are subject to the statutory provisions of 35 USC 112, first paragraph. All that is necessary to satisfy §112 is the statement that a superconducting current can be passed through a transition metal oxides having a  $T_c > 26^\circ\text{K}$ . The Examiner has essentially said this by rejecting applicants non-allowed claims as anticipated under §102(a) or obvious under §103(a) in view of the Asahi Shinbum article. Applicants only allowed claim 136 was allowed over the Asahi Shinbum article because it showed criticality for the formula recited in claim 136. Since Applicants generic teaching does not prevent others from obtaining patents to specific formulas, Applicants are entitled to generic claims to their discovery. Applicants filed this application soon after their discovery. Applicants availed themselves of the one year grace period under 35 USC 102(b) by publishing their results before filing the present

application. This was the quickest way to promote the progress of the field of high  $T_c$  superconductivity which can have substantial societal benefits such as less expensive electric power and more effective medical diagnostic tools. It is a policy of the United States Constitution, which establishes the United States Patent System, to encourage early disclosure of inventions to promote the progress of the useful arts. The Examiner's position that Applicants generic claims are not fully enabled frustrates this policy. Applicants could have decided not to publish Applicants' article and not to file the present application while engaging in years of further experimentation to find all specific examples which had the optimal  $T_c$ . If Applicants acted this way, there would not have been the explosive worldwide effort to fully explore and implement high  $T_c$  transition metal oxide technology. The rationale used by the Examiner is contrary to the Constitutional policy to promote the progress of the useful arts by early disclosure of an invention. Early disclosure should not be a penalty to Applicants. Applicants are pioneers in discovering that transition metal oxides have  $T_c > 26^\circ\text{K}$ . A first discoverer of a wheel whose specific embodiment is a solid disc rotateable about an axle can claim a cylindrical member adapted for rotation about the axle and for rolling on a surface, that is, their discovery. This claim is dominant to a latter inventor's improved wheel comprising spokes which has the advantage of much lighter weight than a disc. The latter inventor is entitled to subservient claim to the dominant claim to a wheel. Applicants are entitled to a dominant claim to their discovery.

The Examiner has not shown by evidence not contained within applicants' teaching that the art of high  $T_c$  superconductors is unpredictable. The Examiner has



attempted to use applicants' teaching to establish such unpredictability. The Examiner has essentially not responded to Applicants' comments. The Examiner has introduced no extrinsic evidence to support the Examiner's opinion that the field of high  $T_c$  superconductivity is unpredictable. The Examiner has not introduced an affidavit qualifying himself to offer such an opinion. The Examiner merely states that his opinion is supported by the record as a whole. The only thing that Examiner relies on is some examples referred to above which do not have  $T_c > 26^\circ\text{K}$  which as stated above is part of Applicants' enabling disclosure.

In response to the resubmitted 1.132 Affidavits of Mitzi, Tsuei and Dinger (filed 12/16/98) and the newly provided 1.132 Affidavits of Thomas Shaw (filed 12/16/98) and Peter Duncombe (filed 12/21/98) the Examiner states:

The Examiner notes the books describing the general principles of ceramic fabrication provided in these Affidavits. Also, the examiner notes that such fabrication techniques were utilized subsequently (after the filing date of the instant application) to produce the superconductive materials described in the Poole et al reference as well as the materials produced by Peter Duncombe (see Affidavit filed 12/21/98).

The affidavit of Peter Duncombe provides notebook entries beginning November 12, 1987, which is prior to Applicants filing date and prior to the Asahi Shinbum article. Duncombe used the general principles of ceramic science to implement the invention

described in Applicants article. Each of the five affiants Tsuei, Mitzi, Duncombe, Shaw and Dinger are experts in the filed of ceramics. Each has stated the Applicants' claimed invention can be implemented based on Applicants teaching and with nothing more than the general principles of ceramic science known at the time of filing of the present application.

The Examiner states:

It is the examiner's maintained position that while general principles of ceramic fabrication were most certainly known prior to the filing date of the instant application, the utilization of such techniques to produce superconductive materials within the scope of the instant claims were not known. The affidavits are not effective to demonstrate enablement at the time of the invention was made. As stated in paper #66, page 8, one may now know of a material that superconduct at more than 26K, but the affidavits do not establish the existence of that knowledge on the filing date of the present application.

The Examiner acknowledges that the fabrication techniques necessary to practice Applicants' invention were known prior to the filing dated of the present application. But the Examiner further states that the "utilization of such techniques to produce superconductive materials within the scope of the instant claims were not known". The scope of the instant claim is flowing a superconductive current in a

transition metal oxide having a  $T_c > 26^\circ\text{K}$ . That is Applicants' discovery. That is why it was not known prior to Applicants' discovery. How to make this type of material was known. Prior to Applicants' discovery, it was not known that they were superconductive with a  $T_c > 26^\circ\text{K}$ . The Examiner incorrectly states "one may now learn of a material that superconducts at more than  $26^\circ\text{K}$ , but the affidavits do not establish the existence of that knowledge on the filing date of the present invention." If that knowledge was known by another prior to the filing date, Applicants would not have a patentable invention since they would not be the initial first and sole inventor. The affidavits state that the knowledge of how to make transition metal oxides by the general principles of ceramic science were known prior to the filing date. In particular, the affidavits of Duncombe and Shaw refer to a number of articles and texts on the general principles of ceramic science. One of these texts is "Structures, Properties and Preparation of Perovskite-type Compounds", F.S. Galasso (1969).

Applicants note that the book "Copper Oxide Superconductors" by Charles P. Poole, Jr., Timir Datta and Horacio A. Farach, John Wiley & Sons (1998) support their position that high temperature superconductors were not difficult to make after their original discovery. This book shall be referred to herein as Poole et al. or the Poole book. The Poole book was published after Applicants' initial discovery which was published in Applicants' article. The Examiner states "[a]s such, it does not, provide evidence of the state of the art at the time the presently claimed invention was made".

Applicants disagree. The preface of this book says "[t]his volume reviews the experimental aspects of the field of oxide superconductivity with transition temperatures from 30K to above 123K, from the time of its discovery by Bednorz and Muller in April, 1986 until a few months after the award of the Nobel Prize to them in October, 1987." Thus the book reports on work done within eighteen months of Applicants' discovery in April 1986 and within eleven months of its publication in September, 1986. In the present application was filed on May 22, 1987. This passage is referring to Applicants and Applicants' article referred to at page 6 of Applicants' specification. This book acknowledges that applicants are the discoverers of the field of high temperature superconductivity. (See Attachment A of Applicants' response dated May 14, 1998 and See Attachment H of Applicants' response dated November 28, 1997). The Examiner's view that the skill of the art was insufficient at the time of the filing date of the present application is untenable in the view of Poole et al. and Applicants' 132 affidavits of Tsuei, Mitzi, Shaw, Dinger and Duncombe, in particular that of Peter Duncombe which reports data prior to the Applicants' filing date.

Applicants note that it is generally recognized that it is not difficult to fabricate transition metal oxides and in particular copper metal oxides that are superconductive after the discovery by applicants that transition metal oxides are high  $T_c$  superconductors. Chapter 5 of the Poole et al. book entitled "Preparation and Characterization of Samples" states at page 59 "[c]opper oxide superconductors with a purity sufficient to exhibit zero resistivity or to demonstrate levitation (Early) are not difficult to synthesize. We believe that this is at least partially responsible for the

explosive worldwide growth in these materials". Poole et al. further states at page 61 "[i]n this section three methods of preparation will be described, namely, the solid state, the coprecipitation, and the sol-gel techniques (Hatfi). The widely used solid-state technique permits off-the-shelf chemicals to be directly calcined into superconductors, and it requires little familiarity with the subtle physicochemical process involved in the transformation of a mixture of compounds into a superconductor." Poole et al. further states at pages 61-62 "[i]n the solid state reaction technique one starts with oxygen-rich compounds of the desired components such as oxides, nitrates or carbonates of Ba, Bi, La, Sr, Ti, Y or other elements. ... These compounds are mixed in the desired atomic ratios and ground to a fine powder to facilitate the calcination process. Then these room-temperature-stable salts are reacted by calcination for an extended period (~20hr) at elevated temperatures (~900°C). This process may be repeated several times, with pulverizing and mixing of the partially calcined material at each step." This is generally the same as the specific examples provided by applicants and as generally described at pages 8, line 19, to page 9, line 5, of Applicants' specification which states "[t]he methods by which these superconductive compositions can be made can use known principals of ceramic fabrication, including the mixing of powders containing the rare earth or rare earth-like, alkaline earth, and transition metal elements, coprecipitation of these materials, and heating steps in oxygen or air. A particularly suitable superconducting material in accordance with this invention is one containing copper as the transition metal." (See Attachment A of Applicants' response dated May 14, 1998 and See Attachment H of Applicants' response dated November 28, 1997).

Consequently, applicants have fully enabled high Tc transition metal oxides and their claims.

As stated in the affidavit of Dr. Mitzi, Dr. Dinger, Dr. Tsuei, Dr. Shaw and Mr. Doncombe the preface of the book by Poole et al., quoted above, the work of Applicants initiated the field of high temperature superconductors and these materials are not difficult to synthesize . And according In re Fisher "it is apparent that such an inventor should be allowed to dominate future patentable inventions of others where those inventions were based in some way on his teaching." (166 USPQ 18, 24)

The Examiner further states:

Moreover, the present claims are directed to processes of using metal oxide superconductors, not processes of making them. Even if the Poole article provided direct evidence of the state of the art at the time the invention was made, which it apparently does not, that evidence still does not pertain to the issue at hand, namely, the process of using metal oxide superconductors to conduct electricity under superconducting conditions.

Applicants disagree. Poole et al. Chapter X entitled "Transport Properties" describes a process of using metal oxides superconductors to conduct electricity under superconducting conditions. Section B of Chapter X is entitled "Current Flow". A copy of Chapter X is in Attachment B of this Appeal Brief.

The Examiner further states in regard to Poole et al.:

(3) Finally, the Preface states in part at A3: "The unprecedented worldwide effort in superconductivity research that has taken place over the past two years has produced an enormous amount of experimental data on the properties of the copper oxide type materials that exhibit superconductivity above the temperature of liquid nitrogen. ... During this period a consistent experimental description of many of the properties of the principal superconducting compounds such as BiSrCaCuO, LaSrCuO, TlBaCaCuO, and YBaCuO has emerged. ... The field of high-temperature superconductivity is still evolving ..." That preface is deemed to show that the field of high-temperature superconductivity continued to grow, on the basis of on-going basic research, after the Bednorz and Meuller article was published.

The continued growth referred to in the passage from Poole et al. quoted above does not mean that this work is not based on Applicants' initial fundamental teaching. Poole et al. as quoted above states that the unprecedented amount of work done in the short period of time after Applicants' work was because the materials "are not difficult to synthesize." Moreover, as quoted above the CCPA In re Fisher states "such an inventor should be allowed to dominate future patentable inventions of other where those inventors were based on in some way on his teachings." Moreover, the referred

to future developments in the passage above are not necessarily patentably distinct from Applicants' teachings. Those who developed these compounds would have a reasonable expectation of success based on Applicants' teaching. The Examiner has provided no evidence to the contrary.

The Examiner acknowledges that the three affidavits of Dr. Tsuei, Dr. Dinger and Dr. Mitzi which were signed in May of 1998 states that the present application "includes all known principles of ceramic fabrication known at the time the application was filed." However, the Examiner further states that the "additional indication also is considered to be a conclusory statement unsupported by particular evidence". The advisory action dated February 25, 1998 acknowledges the revised 1.132 affidavits of Mitzi, Tsuei and Dinger (filed 12/16/98) and the newly provided affidavit of Shaw (filed 12/16/98) and Dumcombe (filed 12/21/98). These revised and additional affidavits cite numerous articles and books, all published before the Applicants' filing date, which provide evidence of the general teaching of ceramic science, and in particular, ceramic fabrication techniques for transition metal oxides, more particularly for Perovskites and most particularly for the type of Perovskites of Applicants' preferred embodiments. Applicants disagree that their affidavits are conclusory. The facts are provided by Poole et al. The affidavits corroborate what Poole et al. states.

Claims 134, 135, and 137-142 were rejected under 35 U.S.C. 112, first paragraph, as based on a disclosure which is not enabling. The Examiner states "[e]ach of claims 134, 135, and 137-142 provide for a superconductor "having a T<sub>c</sub>



greater than 26°K", but those claims do not provide for a step of -- maintaining said (superconductor) at a temperature less than said Tc". These claims have been amended by the amendment after final rejection dated June 14, 1999, to include the steps of maintaining the appropriate temperature for superconductivity as suggested by the Examiner.

In view of these arguments the Board is requested to reverse the Examiner's rejection of claims 24-26, 86-90, 96-113, 129-131, 134, 135-166, 169, 170 and 174-177 as not enabled under 35 USC 112, first paragraph.

## **REJECTIONS UNDER 35 USC 112, SECOND PARAGRAPH**

Claims 86-87, 96-108, 115, 118, 120, 122, 123, 129-135, and 137-142 are rejected under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

In paragraph 6-7 on page 12-16 of the final rejection, Claims 86-87, 96-108, 115, 118, 120, 122, 123, 129-135 and 137-142 have been rejected under 35 USC 112. All changes suggested by the examiner have been made by Amendment after Final Rejection dated June 14, 1999, except for those directed to the terms "layer-like", "perovskite-like", "rare-earth-like", and "layer-type". These terms occur in claims 86-87, 96-108, 112, 113, 117, 118, 122 and 123. As stated by the applicants in the prosecution these are terms of art and well understood by persons of skill in the art.

Claims 143-163 correspond to in claims 86-87, 96-108, 112, 113, 117, 118, 122 and 123. Claims 143-163 have the same wording as claims 86-87, 96-108, 112, 113, 117, 118, 122 and 123 and include all changes suggested by the examiner to overcome rejections of claims 86-87, 96-108, 112, 113, 117, 118, 122 and 123 claims under 35 USC 112, second paragraph.

The Examiner states:

a. With respect to claims 86-87 and 96-108, the terms "layer-type", "perovskite-like", "rare-earth-like" are vague and confusing.

i. The question arises: What is meant by these terms?

(1) The terms "layer-type" and "perovskite-like" are unclear because the "type" or "like" terms are deemed to be indefinite. Terms such as "like", "similar", and "type" are indefinite." It is suggested that "layer-type perovskite-like crystal structure" be changed -- a substantially layered perovskite crystal structure --.

In support of the Examiner's view of term such as "type" and "like", the Examiner cites: Ex parte Remark, 15 USPQ 2d 1498, 1500 (BPAI 1990); Ex parte Kristensen, 10 USPQ 2d 1701, 1703 (BPAI 1989); Ex parte Attig, 7 USPQ 2d 1092, 1093 (BPAI 1988); and Ex parte Copenhaver, 109 USPQ 118 (POBA 1955).

Ex parte Remark is not on point since the Board found the term "and the like" in a claim to be indefinite under §112. Applicants claims do not use this terminology.

Ex parte Kristensen is not on point since the Board found the term "similar" in the phrase "for high pressure cleaning units or similar apparatus" in a claim indefinite under §112, second paragraph. Applicants do not use the terminology "or similar". The Board held with respect to the second paragraph of §112, the inquiry is "to determine

whether the claims do, in fact, set out and circumscribe a particular area with a reasonable degree of precision and particularity". In the present application the terms "perovskite-like", "perovskite-type", "layered-like", "layered-type" and "rare-earth-like" are terms used in the art and these are well known and understood by a person of skill in the art.

Ex parte Attig is also not on point. The Board found the term "ZSM-5-type" indefinite under §112, second paragraph, because the prior art cited during prosecution gave different meanings to the term "ZSM-5-type". But the Board did not find the use of the term "type" in a claim per se indefinite. The Board says "[i]t is true that the zeolites have been defined in various patents and claimed with the terminology "ZSM-5-type". However, clearly the art of record in this case, all of it cited by applicants themselves, in the aggregate serve to render the term indefinite rather than definite". 7 USPQ 1092, 1093. The Examiner has not shown that the terms "perovskite-like", "perovskite-type", "layered-like", "layered-type" and "rare-earth-like" as used in applicants claims have different meanings in different cited prior art. To the contrary, Applicants have shown that these terms have a uniform meaning in the transition metal oxide high T<sub>c</sub> art.

In Ex parte Copenhaver, the Board stated in regard to the terminology "Friedel-Graftz type" catalyst.

"[w]e are of the view that the word "type" when appended to another wise definite expression so extends the scope of such an

expression as to render it objectionably indefinite from the stand point of patent law and procedures."

We are not led to a different conclusion by the fact that the expression may have been used in certain technical and scientific publications which are not subject to the rigid legal requirements for definitions that apply to patent claims. The fact that the expression may have been used in claims of certain patents likewise does not alter our view on the question."

Applicants note that Ex parte Copenhaver decided in 1955 was not cited by the Board in the later Board decisions cited by the Examiner. This decision has not been cited by any other Board or Court decision.

The Examiner states that the term "rare earth-like element" is indefinite and that the terms "type and "like" are unclear. Applicants respectfully disagree. Attachment A of Applicants' response dated November 28, 1997 is the result of a Lexis search done by the undersigned attorney. This search shows the term "rare earth like" or "rare earth and the like" used in 68 US patents. The sections of the 68 patents where these terms appears are printed using the "KWICK" function of Lexis. Attachment B of Applicants' response dated November 28, 1997 is the results of a Lexis search done by the undersigned attorney. This search shows the term "rare earth like" used in the claims of 4 issued US patents. The sections of the claims of the 4 patents where this term appears in the claims are printed using the "KWICK" function of Lexis. Consequently,

the term "rare earth like" is a term use in the art, understood by a person of skill in the art and recognized as a definite term by the USPTO for use in US patent claims.

The Examiner states that the term "perovskite-like" is indefinite. The term "perovskite-like" or "perovskite-type" is commonly used in the art. Attachment C of Applicants' response dated November 28, 1997 is the results of a Lexis search done by the undersigned attorney. This search shows that the terms "perovskite like" and "supercond!" (the "!" represents any combination of letters) are used in 107 US patents. The section of the 107 patents where these terms appears are printed using the "KWICK" function of Lexis. Attachment D of Applicants' response dated November 28, 1997 is a result of a Lexis search done by the undersigned attorney. This search shows the terms "perovskite like" or 'perovskite type" used in the claims of two issued US patents. The sections of the claims of the 2 patents where this term appears in the claims are printed using the "KWICK" function of Lexis. Attachment E of Applicants' response dated November 28, 1997 is a copy of the first page of Chapter 2 of the book "Perovskites and High Tc Superconductors" by F. S. Galasso, Gordon and Breach Scientific Publishers, 1990. Chapter 2 is entitled "Structure of Perovskite-type Compounds". Attachment F of Applicants' response dated November 28, 1997 is a copy of page 78 of the book by C. Poole, Jr. et al. Page 78 is the beginning of the section entitled "D. Perovskite-type Superconducting Structures". The first paragraph of the section states "[i]n their first report on high-temperature superconductors Bednorz and Muller (the applicants) referred to their samples as 'metallic, oxygen deficient ... perovskite like mixed valent copper compounds.' Subsequent work has confirmed that

the new superconductors do indeed have these characteristics. In this section we will comment on their perovskite-like aspects" (insert added). Consequently, the terms "perovskite like" or "perovskite type" are terms used in the art and recognized as a definite by the USPTO for use in US patent claims. (It is noted that this passage also shows that the terminology "mixed valent copper compounds" is used and understood in the art. Applicant further notes that one of the books cited in the affidavit of Peter Duncombe to demonstrate the general teaching of ceramic science includes in the title "Perovskite-Type Compounds". This book was published in 1969 showing that this term was well known and understood by those of the skill in the art long before the filing date of the present application.

The Poole et al. in Chapter VI on "Crystallographic Structures" states at page 73 "[m]uch has been said about the oxide superconductor compounds being **perovskite types**, so we will begin with a description of the perovskite structure." (emphasis added) (See Attachment I of Applicants response dated November 28, 1997).

The undersigned attorney did a search in Lexis for the terms "like" in issued US patents. As shown in Attachment A of Applicants' response dated December 27, 1997, this search Lexis found 140,058 issued US patents using the terminology "like" in the claims. The USPTO has, therefore, accepted this terminology as definite within the meaning of 35 USC 112. A number of specific examples are provided in Attachments B of Applicants' response dated December 27, 1997, to Attachment J of Applicants'

response dated December 27, 1997, each of which are the results of a similar Lexis search. (Lists of the patent numbers will be provided at the request of the Board.) Attachment B shows that there are 443 issued US patents having the term "diamond like" in the claims. Attachment C of Applicants' response dated December 27, 1997, shows that there are 319 issued US patents having the term "diamond like carbon" in the claims. Attachment D of Applicants' response dated December 27, 1997, shows that there are 10 issued US patents having the term "halogen like" in the claims. Attachment E of Applicants' response dated December 27, 1997, shows that there are 11 issued US patents having the term "oxygen like" in the claims. Attachment F of Applicants' response dated December 27, 1997, shows that there are 79 issued US patents having the term "ceramic like" in the claims. Attachment G of Applicants' response dated December 27, 1997, shows that there are 31 issued US patents having the term "carbon like" in the claims. Attachment H of Applicants' response dated December 27, 1997, shows that there are 5 issued US patents having the term "silicon like" in the claims. Attachment I of Applicants' response dated December 27, 1997, shows that there are 10 issued US patents having the term "nitrogen like" in the claims. Attachment J of Applicants' response dated December 27, 1997, shows that there are 17 issued US patents having the term "copper like" in the claims. In view thereof applicants respectfully request the Board to withdraw the rejection of their claims as indefinite for using the terminology "layer-like", "perovskite like" and "rare-earth-like" since use of the term "like" is recognized as definite under 35 USC 112 by the USPTO.



Also the term "ceramic-like" is a term commonly used in the art. Attachment M of Applicants' response dated November 28, 1997 is the result of a Lexis search performed by the undersigned attorney using the search criteria "ceramic" within one word of "like" and "copper" within one word of "oxide" and "rare" within one word of "earth". This search identified 23 issued US patents. These patents are listed in the attachment using the Lexis KWICK feature which list only those portions of the patents where these terms appear. The search was limited to this criteria since a search on "ceramic" within one word of "like" identified more than 1,000 issued US patents and a search on "ceramic" within one word of "like: in the same document as "copper" within one word of "oxide" identified more than 1000 US patents. It is clear that the term "ceramic like" is well understood in the art and is thus definite.

An affidavit under 37 CFR 1.132 of Dr. James W. Leonard, IBM research librarian was submitted on December 15, 1998. Dr. Leonard did a search of articles referencing Applicants article J. G. Bednorz and K. A. Muller, Zeitschrift fur Physik B-Condensed Matter, **64** , pp. 189-193 (Sept. 1986) which is incorporated by reference in the specification at page 6, lines 8-10. As stated at page 6 this article is the basis for applicants invention. More than 5800 articles have referenced applicants' article. This is evidence that applicants' teaching in the present application has motivated persons of skill in the art to work in the field of high  $T_c$  superconductivity and that applicants teaching has fully enabled the invention of their claims. All these articles citing applicants' article acknowledge that their work is based on Applicants' teaching.

Claims 112, 113, 117, 118, 122 and 123 have been rejected under 35 USC 112 as indefinite for using terminology "layer-type". Applicants respectfully disagree.

The undersigned attorney did a search in Lexis for the terms "layer-type" and the term "layer" preceding the term "type" by one word (layer pre/1 type). In this search Lexis found 225 issued US patents using this terminology in the claims. The USPTO has, therefore, accepted this terminology as definite within the meaning of 35 USC 112. Attachment A of the Applicants' response dated December 22, 1998, is the results of this search printed out using the .kw or "kwick" feature which prints the searched term and words before and after the searched term. The searched terminology appears in a number of forms such as "layer type", "layer-type", "layer of type". In view thereof applicants request the Board to reverse the rejection of claims 112, 113, 117, 118, 122 and 123 under 35 USC 112 as indefinite for using the terminology "layer-type".

In attachment B of the Applicants' response dated December 22, 1998, there is a search done by Jim Leonard, an IBM Research librarian, at the request of the undersigned attorney of the term "Layered like" and "layered type" in on-line non-patent literature prior to applicants' filing date. From Attachment B of the Applicants' response dated December 22, 1998, it is clear that these terms are used and understood by persons of skill in the art.

In attachment C of the Applicants' response dated December 22, 1998, there is a search done by Jim Leonard, an IBM Research librarian, at the request of the

undersigned attorney of the term "rare earth like" in on-line non-patent literature prior to applicants' filing date. From this Attachment C it is clear that this term is used and understood by persons of skill in the art. This is in addition to the other evidence of the definiteness of this term to overcome the rejection of applicants' claims as indefinite for using the term "rare earth like" which applicants respectfully request the Board to reverse.

In Attachment D of the Applicants' response dated December 22, 1998, there is a search done by Jim Leonard, an IBM Research librarian, at the request of the undersigned attorney of the term "perovskite like" in on-line non-patent literature prior to Applicants' filing date. From this Attachment D it is clear that this term is used and understood by persons of skill in the art. This is in addition to the other evidence of the definiteness of this term to overcome the rejection of Applicants' claims as indefinite for using the term "perovskite like" which applicants respectfully request the Board to reverse.

The Examiner Further states:

(1) The terms "layer-type" and "perovskite-like" are unclear because the "type" or "like" terms are deemed to be indefinite. Terms such as "like", "similar", and "type" are indefinite." It is suggested that "layer-type perovskite-like crystal structure" be changed -- a substantially layered perovskite crystal structure --.

Applicants have said that person of skill in the art would understand (rare earth-like) to mean that a location occupied by a rare earth element can also be occupied by another element which would have chemical properties similar enough to the rare earth elements such that it would fit in to the lattice site occupied by the rare earth element and act chemically as a rare earth element. To this the Examiner has responded "[t]hat response does not alleviate the problem, however. Other elements may 'fit' into the lattice but they may not necessarily be 'rare-earth-like'". This comment does not address the issue. There are only about 100 elements of which 14 or 15 are rare-earth elements leaving about 86 other elements. It is not difficult for a person of skill in the art to determine which elements will behave like a rare-earth element when placed in the lattice.

Claims 112, 113, 115, 117, 118, 120, 122, and 123 have been found to be indefinite for the reasons that follow.

- i. In claim 112, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.
- ii. In claim 113, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.
- iv. In claim 117, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

v. In claim 118, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

viii. In claim 122, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

ix. In claim 123, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

d. Applicants' arguments filed March 7, 1997 (#59) have been fully considered but they are not persuasive.

These issues have been addressed above.

Applicants have cited numerous issued U.S. patents using "type" and "like" in the claims. Many of these patents used the identical terminology objected to by the Examiner which has been used by Applicants. Many issued U.S. patents similar terminology to that used by Applicants. The Examiner has provided no reason for rejecting Applicants claims using the terminology "layer-type", "perovskite like", "perovskite type" and "rare earth like" under §112, second paragraph as indefinite when there are issued patents using these and related terms in the claims.

In view of these arguments applicants request the Board to reverse the rejection of claims 86-87, 96-108, 115, 118, 120, 122, 123, 129-135, 137-142, 164-169 and 170-177 as being indefinite under 35 U.S.C. § 112, second paragraph.

1.

### **SPECIFIC ARGUMENTS AS TO EACH CLAIM**

In this section of this appeal brief the Asahi Shinbum article is referred to as ASA .

The expression " the Asahi Shinbum article provides no teaching suggestion, motivation for or incentive for the limitations highlighted in the claim language above" is abbreviated as "ASA provides no TSMA for the limitation highlighted in the claim language above". In the rejection of all of applicants claims, except for claim 136, for no enablement under §112, first paragraph, the Examiner has not specifically referred to any of the rejected claims in paragraphs c to f on pages 6 to 12 which is the part of the final rejection directed to the claim rejects under §112, first paragraph. In the objection to the specification under §112, first paragraph the Examiner only refers to claims 24, 88, 96 and 103 . Applicants' comments as to dependent claims include the Applicants' comments as to the claims from which they depend even if not repeated.

The best mode contemplated at the time the present application was filed was the subject of claim 136. Support for each of the claims and how a person of skill in the art can make and use each claim is described above.

#### **Claim 24 recites:**

24. A method including the steps of forming a transition metal oxide having a phase therein which exhibits a superconducting state at a critical temperature in excess of 26°K,

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase, and

passing an electrical supercurrent through said transition metal oxide while it is in said superconducting state.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 25 recites:**

25. The method of claim 24, where said transition metal oxide is comprised of a transition metal capable of exhibiting **multivalent states**.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 26 recites:**

26. The method of claim 24, where said transition metal oxide is comprised of a Cu oxide.

See comments for claim 24.

**Claim 86 recites:**

86. A method, comprising the steps of:

forming a composition including a transition metal, **a rare earth or rare earth-like element, an alkaline earth element, and oxygen, where said composition is a mixed transition metal oxide having a non-stoichiometric amount of oxygen therein** and exhibiting a superconducting state at a temperature greater than 26°K,

maintaining said composition in said superconducting state at a **temperature greater than 26°K**, and

passing an electrical current through said composition while said composition is in said superconducting state.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot



practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art. As to "like" or " type" terminology being indefinite under §112, second paragraph see the discussion above.

**Claim 87 recites:**

87. The method of claim 86, where said transition metal is copper.

See the discussion for claim 86.

**Claim 88 recites**

88. A method, including the steps of:

forming a composition exhibiting a superconductive state at a temperature **in excess of 26°K**, maintaining said composition at a temperature in excess of 26°K at which temperature said composition exhibits said superconductive state, and

passing an electrical current through said composition while said composition is in said superconductive state.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot

practice the invention of this claim from applicants teaching and from what is known to a person of skill in the art.

**Claim 89 recites:**

89. The method of claim 88, where said composition is comprised of a metal oxide.

See the comments for claim 88.

**Claim 90 recites:**

90. The metal of claim 88, where said composition is comprised of a transition metal oxide.

See the comments for claim 88.

**Claim 96 recites:**

96. A superconductive method for causing electric current flow in a superconductive state at a temperature in excess of 26 K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **layer-type** perovskite-like crystal structure, the composition having a superconductor **transition temperature  $T_c$  of greater than 26 K**;

- (b) maintaining the superconductor element at a temperature above 26 K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and
- (c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art. As to “like” or “type” terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 97 recites:**

97. The superconductive method according to claim 96 in which the copper-oxide compound of the superconductive composition **includes at least one rare-earth or rare-earth-like element and at least one alkaline-earth element.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot

practice the invention of this claim from applicants teaching and from what is known to a person of skill in the art. As to “like” or “type” terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 98 recites:**

98. The superconductive method according to claim 97 in which the rare-earth or rare-earth-like element is lanthanum.

See comments for claim 97.

**Claim 99 recites:**

99. The superconductive method according to claim 97 in which the alkaline-earth element is barium.

See comments for claim 97.

**Claim 100 recites:**

100. The superconductive method according to claim 96 in which the copper-oxide compound of the superconductive composition includes **mixed valent copper ions**.

In addition to the comments on claim 96, as the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 101 recites:**

101. The superconductive method according to claim 100 in which the **copper-oxide compound includes at least one element in a nonstoichiometric atomic proportion.**

In addition to the comments on claim 100. As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 102 recites:**

102. The superconductive method according to claim 101 in which **oxygen is present in the copper-oxide compound in a nonstoichiometric atomic proportion.**

In addition to the comments on claim 101, as the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 103 recites:**

103. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a

copper-oxide compound having a **layer-type** perovskite-like crystal structure, the copper-oxide compound **including at least one rare-earth or rare-earth-like element and at least one alkaline-earth element**, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26 K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art. As to “like” or “type” terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 104 recites:**

104. The superconductive method according to claim 103 in which the rare-earth or rare-earth-like element is lanthanum.

See comments on claim 103.

**Claim 105 recites:**

105. The superconductive method according to claim 103 in which the alkaline-earth element is barium.

See comments on claim 103.

**Claim 106 recites:**

106. The superconductive method according to claim 103 in which the copper-oxide compound of the superconductive composition includes **mixed valent copper ions**.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art. As to "like" or " type" terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 107 recites:**

107. The superconductive method according to claim 106 in which the copper-oxide compound includes at least one element in a **nonstoichiometric atomic proportion**.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art. As to “like” or “ type” terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 108 recites:**

108. The superconductive method according to claim 107 in which oxygen is present in the copper-oxide compound in a **nonstoichiometric atomic proportion**.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art. As to “like” or “ type” terminology being indefinite under §112, second paragraph, see the discussion above.



**Claim 109 recites:**

109. A method including the steps of forming copper oxide having a phase therein which exhibits a superconducting state at **a critical temperature in excess of 26°K;**

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said superconducting state;

said copper oxide includes **at least one element selected from the group consisting of a Group II A element, a rare earth element and a Group III B element.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 110 recites:**

110. A method comprising the steps of:

forming a composition including copper, oxygen and an element selected from the group consisting of a Group II A element, a rare earth element and a Group III B element, where **said composition is a mixed copper oxide having a non-stoichiometric amount of oxygen therein** and exhibiting a superconducting state **at a temperature greater than 26°K;**

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 111 recites:**

111. A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature  
**in excess of 26°K;**

maintaining said composition at a temperature in excess of 26°K at which  
temperature said composition exhibits said superconductive state;

passing an electrical current through said composition while said  
composition is in said superconductive state; and

said composition including a copper oxide and an element selected from  
the group consisting of Group II A element, a rare earth element and a  
Group III B element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 112 recites:**

112. A superconductive method for causing electric-current flow in a  
superconductive state at a temperature in excess of 26°K, comprising:

- (a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **layer-type** perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  **of greater than 26°K**, said superconductive composition includes **at least one element selected from the group consisting of a Group II A element, a rare earth element; and a Group III B element;**
- (b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and
- (c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art. As to “like” or “ type” terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 113 recites:**

113. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

- (a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having **a layer-type** perovskite-like crystal structure, the copper-oxide compound including **at least one element selected from the group consisting of a Group II A element, a rare earth element and a Group III B element**, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;
- (b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and
- (c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph

the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is known to a person of skill in the art. As to "like" or "type" terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 114 recites:**

114. A method including the steps of forming copper oxide having a phase therein which exhibits a superconducting state at a critical temperature **in excess of 26°K;**

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said superconducting state;

**said copper oxide includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 115 recites:**

115. A method comprising the steps of:

**forming a composition including copper, oxygen and an element selected from the group consisting of at least one Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, where said composition is a mixed copper oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K;**

**maintaining said composition in said superconducting state at a temperature greater than 26°K; and**

**passing an electrical current through said composition while said composition is in said superconducting state.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 116 recites:**

116. A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature  
**in excess of 26°K;**

maintaining said composition at a temperature in excess of 26°K at which  
temperature said composition exhibits said superconductive state;

passing an electrical current through said composition while said  
composition is in said superconductive state; and

**said composition including a copper oxide and at least one element  
selected from the group consisting of Group II A and at least one  
element selected from the group consisting of a rare earth element  
and a Group III B element.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 117 recites:**

117. A superconductive method for causing electric-current flow in a  
superconductive state at a temperature **in excess of 26°K**, comprising:



(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **layer-type** perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition **includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;**

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 118 recites:**

118. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **layer-type** perovskite-like crystal structure, the copper-oxide compound **including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element**, the composition having a superconductive/resistive transition defining a superconductive-resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to “like” or “type” terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 119 recites:**

119. A method including the steps of forming a transition metal oxide having a phase therein which exhibits a superconducting state at a critical temperature **in excess of 26°K;**

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said superconducting state;

**said transitional metal oxide includes at least one element selected from the group consisting of a Group II A element and at lest one element selected from the group consisting of a rare earth element and a Group III B element.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 120 recites:**

120. A method comprising the steps of:

forming a composition including a transition metal, **oxygen and an element selected from the group consisting of at least one Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element**, where said composition is a mixed transitional metal oxide formed from said transition metal and said oxygen, said mixed transition metal oxide **having a non-stoichiometric amount of oxygen** therein and exhibiting a superconducting state at a **temperature greater than 26°K**;

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to “like” or “type” terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 121 recites:**

121. A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature  
**in excess of 26°K;**

maintaining said composition at a temperature in excess of 26°K at which  
temperature said composition exhibits said superconductive state;

passing an electrical current through said composition while said  
composition is in said superconductive state; and

**said composition including a transitional metal oxide and at least  
one element selected from the group consisting of Group II A  
element and at least one element selected from the group consisting  
of a rare earth element and a Group III B element.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation  
highlighted in the claim language above.

**Claim 122 recites:**

122. A superconductive method for causing electric-current flow in a  
superconductive state at a temperature **in excess of 26°K**, comprising:

(a) providing a superconductor element made of a superconductive  
composition, the superconductive composition consisting essentially of a

transition metal oxide compound having a **layer-type** perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes **at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;**

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to “like” or “type” terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 123 recites:**

123. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal-oxide compound having a **layer-type** perovskite-like

crystal structure, the transition metal-oxide compound including **at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element**, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  **$T_c$  being greater than 26°K**;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to “like” or “type” terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 124 recites:**

124. A method including the steps of forming copper oxide having a phase therein which exhibits a superconducting state at a critical temperature **in excess of 26°K;**

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said superconducting state;

said copper oxide includes at least **one element selected from group consisting of a Group II A element, at least one element selected from the group consisting of a rare earth element and at least one element selected from the group consisting of a Group III B element.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 125 recites:**

125. A method comprising the steps of:



forming a composition including **copper, oxygen and an element selected from the group consisting of at least one Group II A element and at least one element selected from the group consisting of a rare earth element at least one element selected from the group consisting of a Group III B element, where said composition is a mixed copper oxide having a non-stoichiometric** amount of oxygen therein and exhibiting a superconducting state at a temperature **greater than 26°K;**

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 126 recites:**

126. A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature **in excess of 26°K;**

maintaining said composition at a temperature in excess of 26°K at which temperature said composition exhibits said superconductive state;

passing an electrical current through said composition while said composition is in said superconductive state; and

said composition including a copper oxide **and at least one element selected from the group consisting of Group II A element, at least one element selected from the group consisting of a rare earth element and at least one element selected from the group consisting of a Group III B element.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 127 recites:**

127. A superconductive method for causing electric-current flow in a superconductive state at a temperature **in excess of 26°K, comprising:**

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting

essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition **includes at least one element selected from the group consisting of a Group II A element, at least one element selected from the group consisting of a rare earth element and at least one element selected from the group consisting of a Group III B element;**

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 128 recites:**

128. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a

copper-oxide compound having a **layer-type** perovskite-like crystal structure, the copper-oxide compound including **at least one element selected from the group consisting of a group II A element, at least one element selected from the group consisting of a rare earth element and at least one element selected from the group consisting of a Group III B element**, the composition having a superconductive-resistive transition temperature defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 129 recites:**

129. A method comprising providing a composition having a transition temperature **greater than** 26°K, the composition including a rare earth or alkaline earth element, a transition metal element capable of exhibiting **multivalent states** and oxygen, including at least one phase that exhibits superconductivity at temperature in excess of 26°K, maintaining said composition at said temperature to exhibit said superconductivity and passing an electrical superconducting current through said composition with said phrase exhibiting said superconductivity.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 130 recites:**

130. A method comprising providing a superconducting transition metal oxide having a superconductive onset temperature **greater than** 26°K, maintaining said superconducting transition metal oxide at a temperature less than said superconducting onset temperature and flowing a superconducting current therein.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 131 recites:**

131. A method comprising providing a superconducting copper oxide having a superconductive onset temperature **greater than 26°K**, maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a superconducting current in said superconducting oxide.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 132 recites:**

132. A method comprising providing a superconducting oxide composition having a superconductive onset temperature **greater than 26°K**, maintaining said superconducting copper oxide at a temperature

less than said superconducting onset temperature and flowing a superconducting current therein, said composition comprising at least one each of rare earth, an alkaline earth, and copper.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 133 recites:**

133. A method comprising providing a superconducting oxide composition having a superconductive onset **temperature greater than 26°K**, maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a superconducting electrical current therein, said composition comprising at least one each of a Group III B element, an alkaline earth, and copper.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 134 recites:**

134. A method comprising flowing a superconducting electrical current in a transition metal oxide having a  $T_c$  **greater than 26°K** and maintaining said transition metal oxide at a temperature less than said  $T_c$ .

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 135 recites:**

135. A method comprising flowing a superconducting current in a copper oxide having a  $T_c$  **greater than 26°K** and maintaining said copper oxide at a temperature less than said  $T_c$ .

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.



**Claim 136 is allowed.**

**Claim 137 recites:**

137. A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  **greater than 26°K**, said composition comprising at least one each of a III B element, an alkaline earth, and copper oxide and maintaining said composition of matter at a temperature less than  $T_c$ .

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 138 recites:**

138. A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  **greater than 26°K**, said composition comprising at least one each of a rare earth, alkaline earth, and copper oxide and maintaining said composition of matter at a temperature less than said  $T_c$ .

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 139 recites:**

139. A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  **greater than 26°K**, said composition comprising at least one each of a rare earth, and copper oxide and maintaining said composition of matter at a temperature less than said  $T_c$ .

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 140 recites:**

140. A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  **greater than 26°K** carrying, said composition comprising at least one each of a III B element, and copper

oxide and maintaining said composition of matter at a temperature less than said  $T_c$ .

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 141 recites:**

141. A method comprising flowing a superconducting electrical current in a transition metal oxide comprising a  $T_c > 26^\circ\text{K}$  and maintaining said transition metal oxide at a temperature less than said  $T_c$ .

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 142 recites:**

142. A method comprising flowing a superconducting electrical current in a copper oxide composition of matter comprising a  $T_c > 26^\circ\text{K}$  and

maintaining said copper oxide composition of matter at a temperature less than said  $T_c$ .

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 143 recites:**

143. A method, comprising the steps of:

forming a composition including a transition metal, a group IIIB element, an alkaline earth element, and oxygen, where said composition is a **mixed transition metal oxide having a non-stoichiometric amount of oxygen** therein and exhibiting a superconducting state at a temperature **greater than 26°K,**

maintaining said composition in said superconducting state at a temperature greater than 26°K, and

passing an electrical current through said composition while said composition is in said superconducting state.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 144 recites:**

144. The method of claim 143, where said transition metal is copper.

See comments for claim 143.

**Claim 154 recites:**

145. A superconductive method for causing electric current flow in a superconductive state at a temperature **in excess of 26 K**, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **substantially layered** perovskite crystal structure, the composition having a superconductor transition temperature  $T_c$  of greater than 26 K;

b) maintaining the superconductor element at a temperature above 26 K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 146 recites:**

146. The superconductive method according to claim 145 in which the copper-oxide compound of the superconductive composition includes **at least one element selected from the group consisting of a rare-earth element and a Group III B element and at least one alkaline-earth element.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 147 recites:**

147. The superconductive method according to claim 146 in which the rare-earth or rare-earth-like element is lanthanum.

See the comments as to claim 146 and as to “like” or “type” terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 148 recites:**

148. The superconductive method according to claim 146 in which the alkaline-earth element is barium.

See comments as to claim 46.

**Claim 149 recites:**

149. The superconductive method according to claim 145 in which the copper-oxide compound of the superconductive composition includes **mixed valent copper ions**.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 150 recites:**

150. The superconductive method according to claim 149 in which the copper-oxide compound includes at least one element in a **nonstoichiometric atomic proportion**.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 151 recites:**

151. The superconductive method according to claim 150 in which oxygen is present in the copper-oxide compound in a **nonstoichiometric atomic proportion**.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.



**Claims 152 recites:**

152. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **substantially layered** perovskite crystal structure, the copper-oxide compound **including at least one element selected from the group consisting of a rare-earth element and a Group III B element and at least one alkaline-earth element**, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  **being greater than 26 K**;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is known to a person of skill in the art.

**Claim 153 recites:**

153. The superconductive method according to claim 152 in which said at least one element is lanthanum.

See comments as to claim 152.

**Claim 154 recites:**

154. The superconductive method according to claim 152 in which the alkaline-earth element is barium.

See comments as to claim 152.

**Claim 155 recites:**

155. The superconductive method according to claim 152 in which the copper-oxide compound of the superconductive composition **includes mixed valent copper ions.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 156 recites:**

156. The superconductive method according to claim 155 in which the copper-oxide compound includes at least one element in a **nonstoichiometric atomic proportion**.

In addition to comments on claim 155 , as the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 157 recites:**

157. The superconductive method according to claim 156 in which oxygen is present in the copper-oxide compound in a **nonstoichiometric atomic proportion**.

In addition to comments on claim 156, as the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 158 recites:**

158. A superconductive method for causing electric-current flow in a superconductive state at a temperature **in excess of 26°K**, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **substantially layered** perovskite crystal structure, the composition having a superconductive transition temperature **T<sub>c</sub> of greater than 26°K**, said superconductive composition includes **at least one element selected from the group consisting of a Group II A element, a rare earth element; and a Group III B element;**

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature T<sub>c</sub> of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 159 recites:**

159. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **substantially layered** perovskite crystal structure, the copper-oxide compound including **at least one element selected from the group consisting of a Group II A element, a rare earth element and a Group III B element**, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  **$T_c$  being greater than 26°K;**

- (b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and
- (c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claims 160 recites:**

160. A superconductive method for causing electric-current flow in a superconductive state at a temperature **in excess of 26°K**, comprising:

- (a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **substantially layered** perovskite crystal structure, the composition having a superconductive transition temperature  **$T_c$  of greater than 26°K**, said superconductive composition includes **at least one element selected from the group consisting of a**

**Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;**

(b) maintaining the superconductor element at a temperature above 26 °K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 161 recites:**

161. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **substantially layered** perovskite crystal structure, the copper-oxide **compound including at least one element**

selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive-resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 162 recites:**



162. A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal oxide compound having a substantially layered perovskite crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group **consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;**

(b) maintaining the superconductor element at a temperature **above 26°K** and below the superconductor transition  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 163 recites:**

163. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal-oxide compound having a **substantially layered** perovskite crystal structure, the transition metal-oxide compound including **at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element**, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  **being greater than 26°K**;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 164 recites:**

164. A method according to claim 129 wherein said composition comprises a **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 165 recites:**

165. A method according to claim 130 wherein said superconducting transistor metal oxide comprises a **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation

highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 166 recites:**

166. A method according to claim 131 wherein said superconducting copper oxide comprises a **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 167 recites:**

167. A method according to claim 132 wherein said superconducting oxide composition comprises a substantially layered perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph

the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 168 recites:**

168. A method according to claim 133 wherein said superconducting oxide composition comprises a substantially **layered perovskite** crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 169 recites:**

169. A method according to claim 134 wherein said transistor metal oxide comprises a **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot

practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 170 recites:**

170. A method according to claim 135 wherein said copper oxide comprises a **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 171 recites:**

171. A method according to claim 136 wherein said composition comprises a **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 172 recites:**

172. A method according to claim 137 wherein said composition of matter comprises a **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 173 recites:**

173. A method according to claim 138 wherein said composition of matter comprises **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 174 recites:**

174. A method according to claim 139 wherein said composition of matter comprises a **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 175 recites:**

175. A method according to claim 140 wherein said composition of matter comprises **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 176 recites**

176. A method according to claim 141 wherein said transistor metal oxide comprises **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph



the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 177 recites:**

177. A method according to claim 142 wherein said copper oxide composition comprises **substantially layered** perovskite crystal structure

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

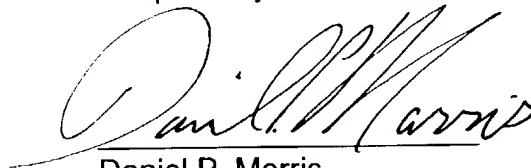
## CONCLUSION

In view of the argument herein, Applicants request the Board:

1. reverse the determination that claims 24-26, 86-90, 96-135 and 137-177 are not supported by the priority document;
2. reverse the rejection of claims 24-26, 86-90, 96-135 and 137-177 as anticipated under 35 USC 102(a) by the Asahi Shinbum article;
3. reverse the rejection of claims 24-26, 86-90, 96-135 and 137-177 as obvious under 35 USC 103(a) in view of the Asahi Shinbum article;
4. reverse the rejection of claims 24-26, 86-90, 96-135 and 137-142 as not enabled under 35 USC 112, first paragraph; and
5. reverse the rejection of claims 86-87, 96-108, 115, 118, 120, 122, 123, 124, 129-135 and 137-142 indefinite under 35 USC 112 second paragraph.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

Respectfully submitted,



Daniel P. Morris  
Reg. No. 32,053  
(914) 945-3217

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598

**APPENDIX**  
**CLAIMS**

24. A method including the steps of forming a transition metal oxide having a phase therein which exhibits a superconducting state at a critical temperature in excess of 26°K,

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase, and

passing an electrical supercurrent through said transition metal oxide while it is in said superconducting state.

25. The method of claim 24, where said transition metal oxide is comprised of a transition metal capable of exhibiting multivalent states.

26. The method of claim 24, where said transition metal oxide is comprised of a Cu oxide.

86. A method, comprising the steps of:

forming a composition including a transition metal, a rare earth or rare earth-like element, an alkaline earth element, and oxygen, where said composition is a mixed

transition metal oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K,

maintaining said composition in said superconducting state at a temperature greater than 26°K, and

passing an electrical current through said composition while said composition is in said superconducting state.

87. The method of claim 86, where said transition metal is copper.

88. A method, including the steps of:

forming a composition exhibiting a superconductive state at a temperature in excess of 26°K, maintaining said composition at a temperature in excess of 26°K at which temperature said composition exhibits said superconductive state, and

passing an electrical current through said composition while said composition is in said superconductive state.

89. The method of claim 88, where said composition is comprised of a metal oxide.

90. The metal of claim 88, where said composition is comprised of a transition metal oxide.

96. A superconductive method for causing electric current flow in a superconductive state at a temperature in excess of 26 K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the composition having a superconductor transition temperature  $T_c$  of greater than 26 K;

(b) maintaining the superconductor element at a temperature above 26 K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

97. The superconductive method according to claim 96 in which the copper-oxide compound of the superconductive composition includes at least one rare-earth or rare-earth-like element and at least one alkaline-earth element.

98. The superconductive method according to claim 97 in which the rare-earth or rare-earth-like element is lanthanum.

99. The superconductive method according to claim 97 in which the alkaline-earth element is barium.

100. The superconductive method according to claim 96 in which the copper-oxide compound of the superconductive composition includes mixed valent copper ions.

101. The superconductive method according to claim 100 in which the copper-oxide compound includes at least one element in a nonstoichiometric atomic proportion.

102. The superconductive method according to claim 101 in which oxygen is present in the copper-oxide compound in a nonstoichiometric atomic proportion.

103. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the copper-oxide compound including at least one rare-earth or rare-earth-like element and at least one alkaline-earth element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26 K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

104. The superconductive method according to claim 103 in which the rare-earth or rare-earth-like element is lanthanum.

105. The superconductive method according to claim 103 in which the alkaline-earth element is barium.

106. The superconductive method according to claim 103 in which the copper-oxide compound of the superconductive composition includes mixed valent copper ions.

107. The superconductive method according to claim 106 in which the copper-oxide compound includes at least one element in a nonstoichiometric atomic proportion.

108. The superconductive method according to claim 107 in which oxygen is present in the copper-oxide compound in a nonstoichiometric atomic proportion.

109. A method including the steps of forming copper oxide having a phase therein which exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said superconducting state;

said copper oxide includes at least one element selected from the group consisting of a Group II A element, a rare earth element and a Group III B element.

110. A method comprising the steps of:

forming a composition including copper, oxygen and an element selected from the group consisting of a Group II A element, a rare earth element and a Group III B element, where said composition is a mixed copper oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K;

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.



111. A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature in excess of 26°K;

maintaining said composition at a temperature in excess of 26°K at which temperature said composition exhibits said superconductive state;

passing an electrical current through said composition while said composition is in said superconductive state; and

said composition including a copper oxide and an element selected from the group consisting of Group II A element, a rare earth element and a Group III B element.

112. A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element, a rare earth element; and a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

113. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a Group II A element, a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

114. A method including the steps of forming copper oxide having a phase therein which exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said superconducting state;

said copper oxide includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element.

115. A method comprising the steps of:

forming a composition including copper, oxygen and an element selected from the group consisting of at least one Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, where said composition is a mixed copper oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K;

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

116. A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature in excess of 26°K;

maintaining said composition at a temperature in excess of 26 °K at which temperature said composition exhibits said superconductive state;

passing an electrical current through said composition while said composition is in said superconductive state; and

said composition including a copper oxide and at least one element selected from the group consisting of Group II A and at least one element selected from the group consisting of a rare earth element and a Group III B element.

117. A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

118. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition

defining a superconductive-resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

119. A method including the steps of forming a transition metal oxide having a phase therein which exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said superconducting state;

said transitional metal oxide includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element.

120. A method comprising the steps of:

forming a composition including a transition metal, oxygen and an element selected from the group consisting of at least one Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, where said composition is a mixed transitional metal oxide formed from said transition metal and said oxygen, said mixed transition metal oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K;

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

121. A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature in excess of 26°K;

maintaining said composition at a temperature in excess of 26°K at which temperature said composition exhibits said superconductive state;

passing an electrical current through said composition while said composition is in said superconductive state; and

said composition including a transitional metal oxide and at least one element selected from the group consisting of Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element.

122. A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal oxide compound having a layer-type perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;



(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

123. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal-oxide compound having a layer-type perovskite-like crystal structure, the transition metal-oxide compound including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

124. A method including the steps of forming copper oxide having a phase therein which exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said superconducting state;

said copper oxide includes at least one element selected from group consisting of a Group II A element, at least one element selected from the group consisting of a rare earth element and at least one element selected from the group consisting of a Group III B element.

125. A method comprising the steps of:

forming a composition including copper, oxygen and an element selected from the group consisting of at least one Group II A element and at least one element selected from the group consisting of a rare earth element at least one element selected from the group consisting of a Group III B element, where said composition is a mixed

copper oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K;

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

126. A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature in excess of 26°K;

maintaining said composition at a temperature in excess of 26°K at which temperature said composition exhibits said superconductive state;

passing an electrical current through said composition while said composition is in said superconductive state; and

said composition including a copper oxide and at least one element selected from the group consisting of Group II A element, at least one element selected from the group

consisting of a rare earth element and at least one element selected from the group consisting of a Group III B element.

127. A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting

essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element, at least one element selected from the group consisting of a rare earth element and at least one element selected from the group consisting of a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

128. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a group II A element, at least one element selected from the group consisting of a rare earth element and at least one element selected from the group consisting of a Group III B element, the composition having a superconductive-resistive transition temperature defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

129. A method comprising providing a composition having a transition temperature greater than 26°K, the composition including a rare earth or alkaline earth element, a transition metal element capable of exhibiting multivalent states and oxygen, including at least one phase that exhibits superconductivity at temperature in excess of 26°K,

maintaining said composition at said temperature to exhibit said superconductivity and passing an electrical superconducting current through said composition with said phrase exhibiting said superconductivity.

130. A method comprising providing a superconducting transition metal oxide having a superconductive onset temperature greater than 26°K, maintaining said superconducting transition metal oxide at a temperature less than said superconducting onset temperature and flowing a superconducting current therein.

131. A method comprising providing a superconducting copper oxide having a superconductive onset temperature greater than 26°K, maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a superconducting current in said superconducting oxide.

132. A method comprising providing a superconducting oxide composition having a superconductive onset temperature greater than 26°K, maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a superconducting current therein, said composition comprising at least one each of rare earth, an alkaline earth, and copper.

133. A method comprising providing a superconducting oxide composition having a superconductive onset temperature greater than 26°K, maintaining said

superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a superconducting electrical current therein, said composition comprising at least one each of a Group III B element, an alkaline earth, and copper.

134. A method comprising flowing a superconducting electrical current in a transition metal oxide having a  $T_c$  greater than 26°K and maintaining said transition metal oxide at a temperature less than said  $T_c$ .

135. A method comprising flowing a superconducting current in a copper oxide having a  $T_c$  greater than 26°K and maintaining said copper oxide at a temperature less than said  $T_c$ .

136. A method comprising the steps of:

forming a composition of the formula  $Ba_xLa_{x-5}Cu_5O_y$ , wherein x is from about 0.75 to about 1 and y is the oxygen deficiency resulting from annealing said composition at temperatures from about 540°C to about 950°C and for times of about 15 minutes to about 12 hours, said composition having a metal oxide phase which exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said composition at a temperature less than said critical temperature to induce said superconducting state in said metal oxide phase; and

passing an electrical current through said composition while said metal oxide phase is in said superconducting state.

137. A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  greater than 26°K, said composition comprising at least one each of a III B element, an alkaline earth, and copper oxide and maintaining said composition of matter at a temperature less than  $T_c$ .

138. A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  greater than 26°K, said composition comprising at least one each of a rare earth, alkaline earth, and copper oxide and maintaining said composition of matter at a temperature less than said  $T_c$ .

139. A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  greater than 26°K, said composition comprising at least one each of a rare earth, and copper oxide and maintaining said composition of matter at a temperature less than said  $T_c$ .

140. A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  greater than 26°K carrying, said composition comprising at least one each of a III B element, and copper oxide and maintaining said composition of matter at a temperature less than said  $T_c$ .



141. A method comprising flowing a superconducting electrical current in a transition metal oxide comprising a  $T_c > 26^\circ\text{K}$  and maintaining said transition metal oxide at a temperature less than said  $T_c$ .

142. A method comprising flowing a superconducting electrical current in a copper oxide composition of matter comprising a  $T_c > 26^\circ\text{K}$  and maintaining said copper oxide composition of matter at a temperature less than said  $T_c$ .

143. A method, comprising the steps of:

forming a composition including a transition metal, a group IIIB element, an alkaline earth element, and oxygen, where said composition is a mixed transition metal oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than  $26^\circ\text{K}$ ,

maintaining said composition in said superconducting state at a temperature greater than  $26^\circ\text{K}$ , and

passing an electrical current through said composition while said composition is in said superconducting state.

144. The method of claim 143, where said transition metal is copper.

145. A superconductive method for causing electric current flow in a superconductive state at a temperature in excess of 26 K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the composition having a superconductor transition temperature  $T_c$  of greater than 26 K;

b) maintaining the superconductor element at a temperature above 26 K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

146. The superconductive method according to claim 145 in which the copper-oxide compound of the superconductive composition includes at least one element selected from the group consisting of a rare-earth element and a Group III B element and at least one alkaline-earth element.

147. The superconductive method according to claim 146 in which the rare-earth or rare-earth-like element is lanthanum.

148. The superconductive method according to claim 146 in which the alkaline-earth element is barium.

149. The superconductive method according to claim 145 in which the copper-oxide compound of the superconductive composition includes mixed valent copper ions.

150. The superconductive method according to claim 149 in which the copper-oxide compound includes at least one element in a nonstoichiometric atomic proportion.

151. The superconductive method according to claim 150 in which oxygen is present in the copper-oxide compound in a nonstoichiometric atomic proportion.

152. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a rare-earth element and a Group III B element and at least one alkaline-earth element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26 K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

153. The superconductive method according to claim 152 in which said at least one element is lanthanum.

154. The superconductive method according to claim 152 in which the alkaline-earth element is barium.

155. The superconductive method according to claim 152 in which the copper-oxide compound of the superconductive composition includes mixed valent copper ions.

156. The superconductive method according to claim 155 in which the copper-oxide compound includes at least one element in a nonstoichiometric atomic proportion.

157. The superconductive method according to claim 156 in which oxygen is present in the copper-oxide compound in a nonstoichiometric atomic proportion.

158. A superconductive method for causing electric-current flow

in a superconductive state at a temperature in excess of 26°K, comprising:

- (a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element, a rare earth element; and a Group III B element;
- (b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and
- (c) causing an electric current to flow in the superconductor element.

159. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

- (a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a Group II A element, a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition

temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

160. A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

161. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive-resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

162. A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

- (a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal oxide compound having a substantially layered perovskite crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;
- (b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition  $T_c$  of the superconductive composition; and
- (c) causing an electric current to flow in the superconductor element.

163. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

- (a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal-oxide compound having a substantially layered perovskite crystal structure, the transition metal-oxide compound including at least one element selected from the group



consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

164. A method according to claim 129 wherein said composition comprises a substantially layered perovskite crystal structure.

165. A method according to claim 130 wherein said superconducting transistor metal oxide comprises a substantially layered perovskite crystal structure.

166. A method according to claim 131 wherein said superconducting copper oxide comprises a substantially layered perovskite crystal structure.

167. A method according to claim 132 wherein said superconducting oxide composition comprises a substantially layered perovskite crystal structure.

168. A method according to claim 133 wherein said superconducting oxide composition comprises a substantially layered perovskite crystal structure.

169. A method according to claim 134 wherein said transistor metal oxide comprises a substantially layered perovskite crystal structure.

170. A method according to claim 135 wherein said copper oxide comprises a substantially layered perovskite crystal structure.

171. A method according to claim 136 wherein said composition comprises a substantially layered perovskite crystal structure.

172. A method according to claim 137 wherein said composition of matter comprises a substantially layered perovskite crystal structure.

173. A method according to claim 138 wherein said composition of matter comprises a substantially layered perovskite crystal structure.

174. A method according to claim 139 wherein said composition of matter comprises a substantially layered perovskite crystal structure.

175. A method according to claim 140 wherein said composition of matter comprises substantially layered perovskite crystal structure.

176. A method according to claim 141 wherein said transistor metal oxide comprises substantially layered perovskite crystal structure.

177. A method according to claim 142 wherein said copper oxide composition comprises substantially layered perovskite crystal structure.

**ATTACHMENT A**

# *Inorganic Chemistry*

AN ADVANCED TEXTBOOK

**THERALD MOELLER**

*Associate Professor of Chemistry  
University of Illinois*

*New York · JOHN WILEY & SONS, Inc.*

*London · CHAPMAN & HALL, Limited*

*Attachment A pages*

COPYRIGHT, 1952

BY  
JOHN WILEY & SONS, INC.

*All Rights Reserved*

*This book or any part thereof must not be reproduced in any form without the written permission of the publisher.*

Library of Congress Catalog Card Number: 52-7487

PRINTED IN THE UNITED STATES OF AMERICA

Emphasis up  
quite generally  
istry, inorganic  
followed by the  
istry, and, sub:  
strongly empha  
More recently,  
inorganic chem  
rather than up  
remarkable the  
and continue to  
position that it

Unfortunately  
expanded in a  
university stud  
their freshman  
courses. These  
dents with the  
them of its sco  
that is to be d  
they have conc  
technology. S  
Sober reflection  
modern and ac

For a number  
semester lectur  
the field from  
existing probl  
advanced und  
At the gradua  
upon which th  
chemistry are  
enrollments ar

Those who l  
suitable textbo  
sequence, they

Attachment A page 2

lathrate com-  
grating). In  
e crystallized  
gly those of  
at ordinary  
components,  
ent to escape.  
sch the com-  
 $\text{CO}_2$ ,  $\text{HCN}$ ,  
( $p\text{-H}_2\text{NC}_6\text{H}_4$ -  
( $\text{C}_6\text{H}_5\text{O}$ ),  $\text{SO}_2$ ,  
gas elements

te compounds  
of importance

ponent. This  
ystal together,  
suitable size,

ay result from  
the crystal or

he time when

terest but are  
sible arrange-  
lead to them is

ts of chemistry.  
n bond forma-  
nd its applica-  
mical combina-  
departure from  
not possess the  
considerations  
on-stoichiomet-  
(1950); *Research*, 1,

ric compounds as opposed to the normal Daltonide or stoichiometric compounds. As examples, one may cite certain metallic hydrides such as  $\text{VH}_{1.56}$ ,  $\text{CeH}_{1.66}$  (p. 411); certain oxides such as  $\text{TiO}_{1.7-1.8}$ ,  $\text{FeO}_{1.066}$ ,  $\text{WO}_{2.88-2.92}$ ; such sulfides, selenides, and tellurides as  $\text{Cu}_{1.7}\text{S}$ ,  $\text{Cu}_{1.6}\text{Se}$ ,  $\text{Cu}_{1.66}\text{Te}$ ,  $\text{CuFeS}_{1.44}$ ; the tungsten bronzes,  $\text{Na}_x\text{WO}_3$ ; etc. Combinations of these types are particularly common among minerals.

Lack of true stoichiometry of this type is associated with so-called *defect crystal lattices*. Defects in a crystal lattice amount to variations from the regularity which characterizes the material as a whole. They are of two types:

1. *Frenkel defects*, in which certain atoms or ions have migrated to interstitial positions some distance removed from the "holes" which they vacated.

2. *Schottky defects*, in which "holes" are left in random fashion throughout the crystal because of migration of atoms or ions to the surface of the material.

Although both types of defect probably characterize crystals of non-stoichiometric compounds, the Schottky defects are the more important. Obviously detectable departure from true stoichiometric composition can result only if serious defects are present. It would follow, therefore, that many apparently stoichiometric compounds are not truly so. If excess metal is present in a crystal, it may also result from partial reduction of high-valent cations; whereas if excess non-metal is present, higher valent cations or lower valent anions than those normally present may be responsible. Many instances are known of multiple oxidation number in a single crystal. Non-stoichiometric compounds often show semi-conductivity, fluorescence, and centers of color. For a comprehensive discussion of this rather complex subject, a detailed review<sup>10</sup> should be consulted.

### SUMMARY OF BOND TYPES

The important linkages which hold together the components of crystalline solids and their general characteristics may be summarized as follows:

1. *Ionic linkages*, in which the crystals are made up of regular geometrical arrangements of positive and negative ions. Such solids tend to possess high melting and boiling points, are hard and difficult to deform, and tend to be soluble in polar solvents. When dissolved in such solvents or fused, they are excellent conductors. Crystals

<sup>10</sup> J. S. Anderson: *Ann. Reports*, 43, 104 (1946).

Attachment A page 3

overcome. Such cage compounds have been called *clathrate compounds*<sup>55</sup> (Latin *clathratus*, enclosed by cross bars of a grating). In general, they occur when mixtures of the components are crystallized under optimum conditions. Their properties are roughly those of the enclosing material. Such compounds are stable at ordinary temperatures with respect to decomposition into their components, but melting or dissolution permits the enclosed component to escape. Examples are hydroquinone compounds which approach the composition  $(C_6H_6O)_n \cdot X$  ( $X = HCl, HBr, H_2S, CH_3OH, SO_2, CO_2, HCN$ , etc.); amine compounds containing sulfurous acid, e.g.  $(p-H_2NC_6H_4-NH_2)_n \cdot H_2SO_3$ ; phenol compounds, e.g.  $(C_6H_5O)_n \cdot SO_2$ ,  $(C_6H_5O)_n \cdot SO_3$ ,  $(C_6H_5O)_n \cdot CO_2$ ; and certain compounds of the inert gas elements (pp. 382-383).

It is obvious that the conditions under which clathrate compounds can form are limited and highly specific. Among those of importance are:

1. An open crystal structure in the enclosing component. This necessitates directed linkages holding the molecule and crystal together, sufficient extension of the groups to form a cavity of suitable size, and a rigid structure.
2. Small access holes to the enclosed cavity. This may result from either proper disposition of groups in the formation of the crystal or sufficient surface area in the enclosing groups.
3. Ready availability of the trapped component at the time when the cavity is closed.

Such compounds are of considerable theoretical interest but are lacking in practical importance. Information on possible arrangements in clathrate compounds and the structures which lead to them is to be found in Powell's discussions.<sup>55</sup>

#### NON-STOICHIOMETRIC COMPOUNDS

The law of definite proportions is one of the basic tenets of chemistry. Its validity is indicated by the restrictions imposed upon bond formation where electrons are involved as already outlined, and its application is generally the assumed basis for any type of chemical combination. There are, however, many instances of apparent departure from this rule among *solid* compounds. Such compounds do not possess the exact compositions which are predicted from electronic considerations alone and are commonly referred to as Berthollide or non-stoichiometric compounds.

<sup>55</sup> H. M. Powell: *J. Chem. Soc.*, 1948, 61; *Endeavour*, 9, 154 (1950); *Research*, 1, 353 (1947-1948).

ric com  
compos  
such as  
 $FeO_{1.05}$   
 $Cu_{1.4}Se$   
Combin  
Lack  
defect c  
from t  
They a

1. F  
interst  
they v
2. S  
throug  
surface

Altl  
stoichi  
tant.  
positio  
theref  
truly  
from  
metal  
those  
know  
stoichi  
and  
comp

TH  
cryst  
stic  
met  
tanc  
zoid  
int

Attachment page 4



*Fundamentals  
of  
chemistry  
a  
modern  
introduction*

---

FRANK BRESCIA

JOHN ARENTS

HERBERT MEISLICH

AMOS TURK

*Department of Chemistry  
The City College of the  
City University of New York*



ACADEMIC PRESS

*New York and London*

*Attachment A page 5*

*The text of this book was set in Monotype  
MODERN 8A printed and bound by The Maple Press Company.  
The book is printed on Thor Cote Plate by Bergstrom Paper  
Company. The binding is Tonero offset cloth,  
Arkwright-Interlaken Inc.  
The design of the text and cover was created by Betty Binns.  
The drawings are by F. W. Taylor.*

COPYRIGHT © 1966, BY ACADEMIC PRESS INC.

All rights reserved.

No part of this book may be reproduced in any form,  
by photostat, microfilm, or any other means, without  
written permission from the publishers.

ACADEMIC PRESS INC.

111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by

ACADEMIC PRESS INC. (LONDON) LTD.

Berkeley Square House, London W.1

Library of Congress catalog card number: 65-26049

First Printing, January, 1966

Second Printing, April, 1966

PRINTED IN THE UNITED STATES OF AMERICA

*Attachment A page 6*

*matter: the mass of a chemically reacting system remains constant.* This law is consistent with the data obtained with the most precise balances available. If matter is created or destroyed, the quantity is less than can be detected with the best available balance.

#### 4.2 THE LAW OF DEFINITE PROPORTIONS

Analyses of compounds show that when elements form a given compound, they always combine in the same ratio by weight. For example, independently of the source or method of formation, silicon dioxide,  $\text{SiO}_2$ , contains 46.7% by weight of silicon and 53.3% of oxygen. This knowledge is summarized in the *law of definite proportions: the weight composition of a given compound is constant.*

**EXAMPLE 1** 10.0 g of silicon dust, Si, is exploded with 100.0 g of oxygen,  $\text{O}_2$ , forming silicon dioxide,  $\text{SiO}_2$ . How many grams of  $\text{SiO}_2$  are formed and how many grams of  $\text{O}_2$  remain uncombined?

**ANSWER** Since 46.7 g of Si combines with 53.3 g of  $\text{O}_2$ , the quantity of  $\text{O}_2$  required per gram of Si is

$$\frac{53.3 \text{ g } \text{O}_2}{46.7 \text{ g Si}}$$

and, therefore, for 10.0 g of Si, the quantity of  $\text{O}_2$  required is

$$10.0 \text{ g Si} \times \frac{53.3 \text{ g } \text{O}_2}{46.7 \text{ g Si}} = 11.4 \text{ g } \text{O}_2$$

Hence, the weight of  $\text{SiO}_2$  formed is  $10.0 \text{ g} + 11.4 \text{ g} = 21.4 \text{ g}$  and the weight of uncombined  $\text{O}_2$  is  $100.0 \text{ g} - 11.4 \text{ g} = 88.6 \text{ g}$ .

#### 4.3 THE ATOMIC THEORY

The weight relationships of substances participating in chemical reactions are clearly explained in terms of the atomic theory. Although John Dalton (1803) is generally recognized as the inventor of the theory, he was anticipated by other scientists, particularly William Higgins (1789). Thus, it appears that the law of multiple proportions (Section 4.4) was foreshadowed by Higgins and Dalton from their respective atomic theories. A verified prediction made by a theory constitutes the strongest argument in its favor. However, the novel and central point of Dalton's activities was the attempt to determine the relative weights of atoms. This goal focused attention upon the theory, and revealed a new field of human endeavor that ultimately made chemistry a systematized body of knowledge.

The assumptions of the atomic theory were

- (i) *The elements are composed of indivisible particles called atoms.*
- (ii) *All the atoms of a given element possess identical properties, for example, mass.*

**ATTACHMENT B**

L. J. WATSON, PRESIDENT, STEEL INDUSTRIES OF AMERICA

# X

## TRANSPORT PROPERTIES

### A. INTRODUCTION

The principal applications of superconductors are based upon their ability to carry electric current without any loss, and therefore it is important to understand their transport properties. This chapter begins with a discussion of resistivity and critical current flow in the absence of externally applied fields. This is followed by a discussion of several techniques involving applied fields and thermal effects. The chapter concludes with sections on tunneling and the Josephson effect.

### B. CURRENT FLOW

Electric currents that flow through a superconductor owing to the action of an external source of potential are called transport currents, and those that arise in an external magnetic field to cancel the magnetic flux inside the superconductor are called diamagnetic screening currents or shielding currents. In magnet applications transport currents are started by an external source and continue to flow (persist) after its removal, while in long-distance electrical transmission applications the source voltage continues to be applied.

Current densities  $J$  are intrinsic properties and hence are more useful than currents  $I$  for quantitative comparisons between different superconductors. Transport current densities can be comparable in magnitude to shielding current densities.

The velocity in these cases is of the value

### 1. Resistivity

A superconductor has a zero resistivity, application of a magnetic field produces sharp diamagnetic screening currents, percolation

Many of the superconducting materials made because of their low  $T_c$  and their susceptibility

Good conductors of electricity are also good conductors of heat. The thermal conductivity of a material is proportional to its resistivity (cf. p. 3 from

Needle superconducting materials are superconductors of the type  $(\text{Sr}_{1-x}\text{La}_x)\text{CuO}_2$  exp[ $(T_0/T_c)^2$ ] resistivity is (Kastner).

The resistivity with the current has been

The velocity of electrons at the Fermi surface  $v_F$  was estimated to be  $10^7$  cm/sec in these materials, which is of the same order as in A-15 compounds, and  $\frac{1}{10}$  of the value in aluminum (Garoc).

### 1. Resistivity

A susceptibility measurement is a better thermodynamic indicator of the superconducting state because magnetization is a thermodynamic state variable. The resistivity, on the other hand, is easier to measure, and can be a better guide for applications. The temperature of zero resistivity shows when continuous superconducting paths are in place between the electrodes. Filimentary paths can produce sharp drops in resistivity at higher temperatures than pronounced onsets of diamagnetism. This can be described in terms of two- and three-dimensional percolation thresholds (see Section III-E).

Many investigators have published figures of resistivity or resistance versus temperature, since this is the most popular way to determine the critical temperature and the sharpness of the transition. It should be remembered that if the specimen is porous, accurate determinations of the resistivity cannot readily be made because of the presence of voids and intergrain problems. In almost all cases  $T_c$  determined from the resistivity midpoint is at a higher temperature than its susceptibility counterpart.

Good conductors such as copper and silver have room-temperature resistivities of about  $1.5 \mu\Omega$  cm, and at liquid nitrogen temperature the resistivity typically decreases by a factor of 6-8, as shown by the data in Table X-1. The elemental superconductors, such as Nd, Pb, and Sn, have room-temperature resistivities a factor of 10 greater than good conductors. The other metallic elements present in oxide superconductors, namely, Ba, Bi, Ca, La, Sr, Tl, and Y, have resistivities 10-80 times that of Cu. The copper oxide superconductors have even higher room-temperature resistivities, over three orders of magnitude greater than that of metallic copper, which puts them within a factor of 3 or 4 of the semiconductor range, as shown by the data in Table X-1. The resistivity of these materials above  $T_c$  decreases more or less linearly with decreasing temperature (cf. Fig. VII-11) down to the neighborhood of  $T_c$ , with a drop by a factor of 2 or 3 from room temperature to this point, as shown by the data in the table.

Needless to say, the concept of resistivity is not a meaningful one to apply to a superconductor below  $T_c$ . Nevertheless, it is instructive to study the low-temperature resistance in nonsuperconducting compounds that are closely related to superconductors. For example, in nonsuperconducting crystals of  $(La_{1-x}Sr_x)_2(Cu_{1-y}Li_y)O_{4-\delta}$  a variable range type of hopping resistance, that is,  $R \approx \exp[(T_0/T)^4]$ , was reported. From this it has been argued that the poor conductivity is not due to a large gap, but rather to localization of the states at  $E_F$  (Kastn).

The resistivity in the high-temperature ( $80 \leq T \leq 1200$  K) region is linear with the temperature for  $T < 600$  K and superlinear above 600 K. This linearity has been linked to the two-dimensional character of the electron transport

Attachment B page 2

TABLE X-1. Examples of Resistivities at Room Temperature  $\rho_{300}$ , at Low Temperature  $\rho(T)$ , and Their Ratio  $\rho_{300}/\rho(T)$ <sup>a</sup>

Material	$\rho_{300}$ ( $\mu\Omega$ cm)	$\rho(T)$ ( $\mu\Omega$ cm)	T (K)	$\rho_{300}/\rho(T)$	Ref.
Cu	1.68	0.18	77	9.3	
Ag	1.60	0.26	77	6.2	
Pt	10.6	1.74	77	6.1	
Sn	12.4				
Nb	12.5				
Tl	18				
Pb	20				
Sr	23				
Ca	53				
Y	57				
La	58				
Ba	60				
Bi	119				
LaSr*	2200	430	44	5.1	Kobay
	2700	850	50	3.2	Penne
	2300	510	50	4.5	Tara1
LaSr (0.05)		950(∥)	40		Hidak
		19000(⊥)	40		Hidak
(0.1)			50	3.6	Coppe
		1600	44		Kobay
LaBa(0.1)	1200				Tonou
YBa*	2000	1000	95	4.0	Coppe
	650	225	95	2.9	Bonn1
	900	470	100	1.9	Caval
	4000	2000	100	2.0	Mawds
		730	120	1.9	Neume
	1350	680	100	2.0	Panso
(∥)	450	200	100	2.3	Penne
(⊥)	13000	18000	100	0.7	Tozer
Y <sub>0.6</sub> Ba <sub>0.4</sub> CuO <sub>3</sub>	1.5 × 10 <sup>6</sup>				Tozer
DyBa*					Tonou
EuBa*	720	410	100	~1.3	Map11
TmBa*	4600	1900	100	1.8	Hikit
YbBa*				2.4	Neume
				~3.3	Map11

<sup>a</sup>Typical semiconductors have values from 10<sup>4</sup> to 10<sup>15</sup>  $\mu\Omega$  cm and insulators range from 10<sup>20</sup> to 10<sup>28</sup>  $\mu\Omega$  cm. The notation ∥ and ⊥ refers to resistivity measurements made parallel to and perpendicular to the Cu-O planes, respectively.

(Micna)  
mean fr  
coupling  
which w  
An ex  
observec  
trons thi  
the temp  
transitio  
the loss  
reflect th

where A  
formula  
rithmic c  
tetragon  
also rep  
The re  
(i.e., alo  
about 20  
CuO. W  
polycryst  
Hyste  
as illustr  
for decre  
width of

## 2. Critic

When th  
current c  
effect. T  
J<sub>c</sub>(0) at  
YBa<sub>2</sub>Cu<sub>3</sub>  
K (e.g.,

The v  
suring th  
sample (c  
uses a  
(Kumak

(Micna). Applying the Mott-Ioffe-Regel rule (minimum scattering length  $<$  mean free path) to the observed normal state resistivity gave electron-phonon couplings in both  $\text{LaSr}^*$  ( $\lambda = 0.1$ ,  $\lambda_{\text{max}} = 0.45$ ) and  $\text{YBa}^*$  ( $\lambda = 0.3$ ,  $\lambda_{\text{max}} = 1.2$ ) which were too small to account for the observed  $T_c$  (Gurv1, Gurv2).

An exponential dependence of the resistivity of  $\text{YBa}^*$  on the temperature was observed between 80 and 1240 K (Fishe). This may occur via tunneling of electrons through barriers. The value of the exponent was different above and below the temperature  $T^*$  (700-750), which is near the tetragonal-to-orthorhombic transition. The temperature dependence of the resistivity appears to result from the loss of oxygen during heating, and the following expression was proposed to reflect this dependence:

$$\rho(T) = \frac{AT}{1 - \delta(T)} \quad (\text{X-1})$$

where  $A$  is temperature insensitive and  $\delta(T)$  is the oxygen content factor in the formula  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (Chaki; see also Fiory). A break in the slope of the logarithmic derivative  $(T/\rho)d\rho/dT$  plotted against  $T$  occurs at the orthorhombic-to-tetragonal phase transition (Fiory). Evidence for an  $n$ -to- $p$  type transition was also reported (Choi1).

The resistivity is much higher when measured perpendicular to the  $ab$  planes (i.e., along the  $c$  axis) than it is parallel to the planes. Measured ratios  $\rho_{\perp}/\rho_{\parallel}$  are about 20 for  $\text{LaSrCuO}$  (Hidak), 50 for  $\text{YBaCuO}$  (Tozer), and  $10^5$  for  $\text{BiSrCaCuO}$ . We see from Table X-1 that typical measured resistivities, which are on polycrystalline specimens, are much closer to the in-plane values.

Hysteresis effects have been seen in the resistance versus temperature curves, as illustrated on Fig. X-1 for  $(\text{Y}_{0.875}\text{Ba}_{0.125})_2\text{CuO}_{4-\delta}$  (Taras). The 2-K shift in  $T_c$  for decreasing and increasing temperature measurements is about half of the width of the transition.

## 2. Critical Current Density

When the current density in a superconductor exceeds a value called the critical current density  $J_c$ , the superconductivity is destroyed. This is called the Silsbee effect. The value of  $J_c(T)$  increases from zero at  $T = T_c$  to a maximum value  $J_c(0)$  at 0 K (Leide). Figure X-2 shows the magnetic field dependence of  $J_c$  for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  from 0.5 to 6 T for several temperatures in the range from 4.2 to 83 K (e.g., Panso; see also Ekinz, Jones).

The value of  $J_c$  can be determined directly by the resistivity method by measuring the current at which a small voltage (typically 1  $\mu\text{V}$ ) is induced across the sample ( $\approx 1$  cm) in a four-probe resistivity arrangement. An indirect method uses a magnetization versus field hysteresis loop through the expression (Kumak, see also Sunzz, Xiao2).

$$J_c = 30 \Delta M/d \quad \text{A/cm}^2 \quad (\text{X-2})$$

ADW

T) Ref.

Kobay  
Penne  
Taral  
Hidak  
Hidak  
Coppe  
Kobay  
Tonou  
Coppe  
Bonn1  
Caval  
Mawds  
Neume  
Panso  
Penne  
Tozer  
Tozer  
Tonou  
Map11  
Hikit  
Neume  
Map11

age from  $10^{20}$  to  $10^{28}$   
o and perpendicular

Attachment B page 3



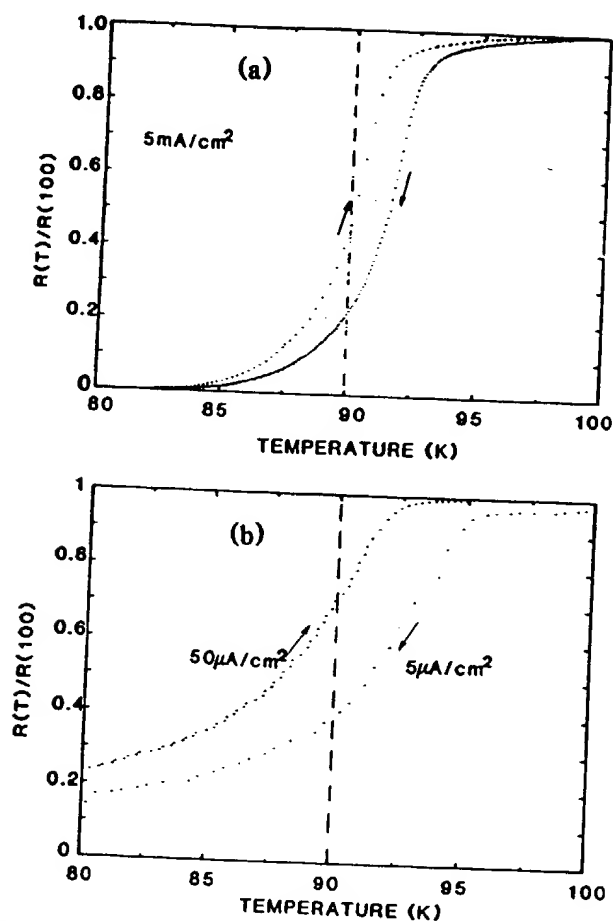


Fig. X-1. Hysteresis of resistance versus temperature for two samples of YBaCuO, for increasing and decreasing temperature, as indicated by the arrows. (a) current density  $5 \text{ mA/cm}^2$ ; (b) current density  $50 \mu\text{A/cm}^2$  for increasing temperature and  $5 \mu\text{A/cm}^2$  for decreasing temperature (Taras).

where  $\Delta M$  is the hysteresis of magnetization per unit volume in electromagnetic units per cubic centimeter and  $d$  is the size of the sample in centimeters.

The  $J_C$  values measured directly are called transport currents and those determined from hysteresis loops are called magnetization currents. Transport currents were found to be smaller than magnetization currents in the LaSrCuO (e.g., Larba) and YBaCuO (e.g., Kuma1, Togan) systems. This could be caused by granularity and intergrain contact, and improving sample quality might bring transport currents closer to their magnetization current counterparts (Wuhlz). In contrast to this, magnetization and transport critical currents of YBa\* epitaxial films were reported to be the same (Chaud, Ohzzz).

Attachment B page 4

Fig. X-  
tained l

Crit  
are list  
Umeza  
have hi  
larger  
densiti  
Jin et a  
as high  
and gr  
and sin  
Gri  
apprec  
curren  
(Hueb  
Giova)

Ver  
filame  
(Chen  
lider a  
 $10^5 \text{ A/}$   
cally s  
applic  
old on  
ity, as

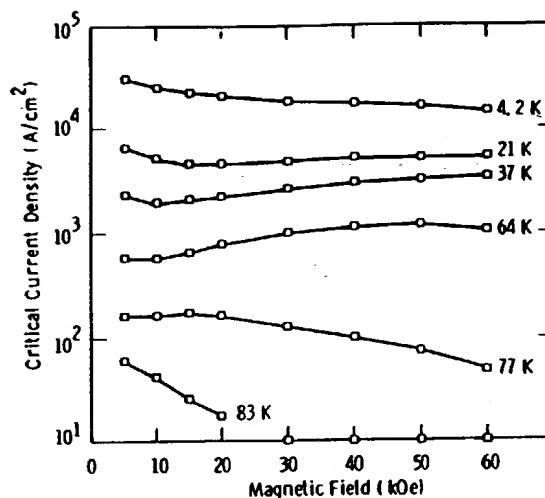


Fig. X-2. Magnetic field dependence of critical current densities of  $\text{YBa}_2\text{Cu}_3\text{O}_{7.4}$  obtained from hysteresis loops (Panso) ( $10 \text{ kG} = 1 \text{ T}$ ).

Critical current densities for a number of  $\text{LaSrCuO}$  and  $\text{YBaCuO}$  materials are listed in Table X-2 (e.g., Camp1, Chau2, Chau3, Daizz, Jinz2, Kagos, Umeza, Xiao2). We see from the table that the  $\text{YBaCuO}$  compounds tend to have higher values of  $J_c$  than  $\text{LaSrCuO}$ . For the same material  $J_c$  is considerably larger at 4.2 K than at 77 K. It is also quite anisotropic, with critical current densities much larger parallel to the Cu-O planes than perpendicular to them. Jin et al. (Palca) employed a technique called melt-textured growth to achieve  $J_c$  as high as  $10^3 \text{ A/cm}^2$  in a magnetic field of 1 T at 77 K. Values of  $J_c = 10^6 \text{ A/cm}^2$  and greater have been reported in epitaxial thin films (Chaud, Kwoz1, Ohzzz) and single crystals (Crabt, Ding1, Wort1).

Grinding and heat treating samples of  $\text{LaSrCuO}$  and  $\text{YBaCuO}$  was found to appreciably increase the critical current density at 4 K (Suena). High critical currents require efficient flux pinning since  $J_c$  increases with the pinning force (Huebe, p. 125). Weak pinning leads to flux creep and low critical currents (e.g., Giova).

Very high values of  $J_c$  are needed for magnet materials. A niobium-titanium filament has been reported with  $J_c$  values as high as  $3.7 \times 10^5 \text{ A/cm}^2$  at 5 T (Cheng). The Superconducting Super Collider and Relativistic Heavy Ion Collider accelerators require 5- $\mu\text{m}$  wire filaments that support  $J_c$  of at least  $2.8 \times 10^5 \text{ A/cm}^2$  in a 5-T magnetic field (Grego). At present  $J_c$  values of technologically suitable oxide materials at 77 K are too small for such high-field magnet applications. Although the oxide superconductors do not yet compete with the old ones in critical currents, they are superior in their critical field ( $H_{c2}$ ) capability, as shown in Fig. I-2.

Attachment B page 5

TABLE X-2. Critical Current Densities<sup>a</sup>

Compound	$J_c$ (A/cm <sup>2</sup> )	T (K)	H (T)	Measurement Method	Comments	Ref.
LaSr*	10 <sup>5</sup>	4		Mg		Suena
LaSr(0.05)	2	4.2	0.025	Tr		Larba
	1	4.2	10 <sup>-3</sup> -3	Tr		Larba
	0.75	4.2	7	Tr		Larba
YBa*	>10 <sup>6</sup>	4.2		Mg	E-film	Chaud
	>10 <sup>5</sup>	77		Mg	E-film	Chaud
	10 <sup>5</sup>	77		Mg	E-film	Chaul
	1.4 × 10 <sup>6</sup> (⊥)	5	0-1	Mg	M-xt	Crabt
	1.4 × 10 <sup>4</sup>	5	0.4	Mg	P-xt	Crabt
	1.1 × 10 <sup>4</sup> (⊥)	77	0.1	Mg	M-xt	Crabt
	4.3 × 10 <sup>3</sup> (⊥)	77	1	Mg	M-xt	Crabt
	1.2 × 10 <sup>2</sup>	77	0.6	Mg	P-xt	Crabt
	4 × 10 <sup>5</sup>	4.5		Mg	M-xt	Dingl
	3 × 10 <sup>4</sup> (⊥)	4.5		Mg	M-xt	Dingl
	>10 <sup>6</sup>	4.5	>4	Mg	M-xt	Dingl
	1-200	0	0	Tr	$J_{c1}/J_{c2} \sim 6$	Ekinz
	620	77	0	Tr	sintered rod	Glowa
	3 × 10 <sup>4</sup>	77	1	Mg	P-xt	Jinzz
	10 <sup>6</sup>	4.2		Tr	E-film, bc plane	Kumak
						Kwozl

10 <sup>3</sup>	77		Tr	E-film, bc plane	Kwozl
1.5-2 × 10 <sup>4</sup>	4.2	1-10	Mg		Larbl
235	77	1	Mg		Larbl
10 <sup>6</sup>	77	6	Mg		Larbl

Attachment to page 6

**Dingi  
Ekinz  
Glowa  
Jinzz  
Kumak  
Kwozi**

M-x  
 $J_{c1}/J_{c2} \sim 6$   
sintered rod  
P-x  
E-film, bc plane

$$\begin{array}{ccccc} & & \text{Mg} & & \\ & & \text{Tr} & & \\ & & \text{Tr} & & \text{Mg} \\ & & \text{Tr} & & \text{Tr} \end{array}$$

40 01

4.5  
0  
77  
77  
4.2

$>10^6$   
 1-200  
 620  
 $3 \times 10^4$   
 $10^6$

E-film, bc plane	Kwozi
	Larbl
	Larbl
	Larbl
E-film	Ohzzz
E-film	Ohzzz
E-film	Ohzzz
	Panso
	Panso
sinter forged	Songz
sinter forged	Songz
	Suena
	Togan
	Togan
M-xt	Worbl
M-xt	Worbl
	Capol
	Caval
pulsed	Iguch
pulsed	Jones
	Jones

**E-film, bc plane**

E-film,  
E-film  
E-film  
E-film

E-film, be pla  
E-film  
E-film  
E-film  
sinter forged  
sinter forged

E-film	E-film	E-film	E-film	sinter	sinter	M-xt	M-xt
--------	--------	--------	--------	--------	--------	------	------

E-film,  
E-film  
E-film  
E-film  
sinter for  
sinter for  
M-xt  
M-xt  
pulsed  
pulsed

Tr Mg Mg Mg Mg Mg Mg Mg Mg Mg Mg Mg Mg Mg Mg Tr Tr Tr Tr Tr

1-10  
1  
6  
0.3  
0  
0.3  
0.1-6  
0.1-6  
0.4  
0.4  
  
0.2  
0.1  
0  
0  
  
0  
0

77 4.2 77 77 4.2 78 78 4.2 77 5 5 4 4.2 77 4.5 4.5 77 77 14 4.2 77

$$10^3, 1.5-2 \times 10^4, 235, 10, 0.9-11 \times 10^5, 1-5 \times 10^4, 0.4-4 \times 10^4, 1.5-3 \times 10^4, 50-200, 9.4 \times 10^4(\perp), 5.9 \times 10^4(\parallel), 10^5, 8 \times 10^3, >10^2, 3.2 \times 10^6(\perp), 1.6 \times 10^4(\parallel), 168, >1100, 14, 2800, 650$$
$$\begin{array}{l} \text{YBa}_2\text{Cu}_3\text{O}_{6.5} \\ \text{YBa}_2\text{Cu}_3\text{O}_{6.9} \\ \text{Y}_{0.8}\text{Ba}_{1.2}\text{CuO}_x \\ \text{YBaCuO} \\ \text{YBaCuO} \end{array}$$

\*E-film, epitaxial film; Mg, magnetization; M-xt, monocrystal; P-xt, polycrystal; Tr, transport. Some measurements were made in the presence of an applied magnetic field  $H$ , and the notation  $\parallel$  and  $\perp$  refers to currents measured with the field applied parallel and perpendicular to the Cu-O planes, respectively.

Attachment B page 7

### 3. Persistent Currents

The zero-resistance property of a superconductor implies that an electrical current flowing in a closed path should persist indefinitely. Several investigators have examined this property and set lower limits on the lifetime of the current and upper limits on its associated resistivity. The lifetime of the persistent or superconducting current in a cylindrical LaSrCuO sample is in excess of  $3 \times 10^6$  sec or more than a month, corresponding to a resistivity of less than  $3 \times 10^{-17} \Omega \text{ cm}$  (Wells). Current lifetimes in loops of low-temperature superconductors are much longer and suggest an effective resistivity of  $< 10^{-23} \Omega \text{ cm}$  (Chand), close to the value of  $7 \times 10^{-23} \Omega \text{ cm}$  reported for YBaCuO (Kedve). Other reported minimum resistivity determinations are:  $< 10^{-9} \Omega \text{ cm}$  (Iguch),  $4 \times 10^{-16} \Omega \text{ cm}$  for  $(\text{Y}_{0.6}\text{Ba}_{0.4})_2\text{CuO}_4$  (Skoln),  $< 10^{-16} \Omega \text{ cm}$  in YBa\* (Tjuka), and  $2 \times 10^{-18} \Omega \text{ cm}$  (Yehzz). Similar results ( $10^{-24} \Omega \text{ cm}$ ) were obtained for TlBaCaCuO.

The ceramic superconductors are granular and the relaxation of trapped field and critical current loops may be characteristic of glassy structures (cf. Section VIII-D-5). Because of the granularity even small fields can penetrate the materials. This property has been utilized to nondestructively read the supercurrent (Macf1).

## C. MISCELLANEOUS TRANSPORT PROPERTIES

In this section we will discuss some transport properties that depend upon the application of electric or magnetic fields, and some that involve thermal effects. Various transport results of YBa\*, namely, thermal conductivity, thermopower, Hall constant, and resistivity, were found to be consistent with ordinary metallic behavior with a strong phonon interaction (Uher2). It was concluded that there is no evidence for exotic electronic behavior in YBa\*.

### 1. Magnetoresistance

A number of investigators have studied the resistance versus temperature behavior in low (Hikam), high (Kwokz, Mats1, Mura1, Uher4), and very high (Ouss1) magnetic fields.

Very high field ( $H \leq 43 \text{ T}$ ) longitudinal and transverse orientation studies of YBa\* (Ouss1) show that the magnetoresistance  $\Delta\rho(T, H) = \rho(T, H) - \rho(T < 0)$  may be decomposed into three contributions

$$\Delta\rho = \Delta\rho^M + \Delta\rho^N + \Delta\rho^S \quad (\text{X-3})$$

where  $\Delta\rho^S (>0)$  is the increase in resistance when the superconducting fluctuations are suppressed by the field,  $\Delta\rho^N$  is the normal or Lorentz magnetoresistance, and  $\Delta\rho^M$  is an unidentified component that may be associated with mag-

netic ordering at 50 K, and critical field

One of the resistivity mobility determinations in m YBaCuO systems downward to susceptibility increase in f

### 2. Hall Effect

The Hall effecters in the n carriers are drop to zero

In this extension of the c field on the an electric f The Hall co

Fig. X-3. T fields from C

Attachment B page 8

netic ordering. No change in the superconductivity was observed when  $H = 43$  T at 50 K, and only  $\approx 50\%$  normal phase resistance was found at 77 K. The upper critical field  $H_{C2}$  was estimated as  $\approx 125$  T.

One of the problems with comparing transport and magnetic  $T_c$  data is that resistivity measurements are generally made in zero magnetic field and susceptibility determinations require the presence of a field. The resistivity measurements in magnetic fields (Kobay, Wuzzz) show that for the LaSrCuO and YBaCuO systems, respectively, the transition temperature broadens and shifts downward by perhaps 1 K/T (Ihar1, Nakao), as shown in Fig. X-3. In an ac susceptibility determination a downward shift of  $T_c$  by 2 K was reported for an increase in field amplitude from 3.1 to 31  $\mu$ T (Odazz).

## 2. Hall Effect

The Hall effect provides information on the sign and the mobility of charge carriers in the normal state, and usually a positive sign indicates that the majority carriers are holes. In the superconducting state the Hall voltage is expected to drop to zero (Hundl, Zhan1).

In this experiment a magnetic field  $H_0$  is applied perpendicular to the direction of the current flow through the sample. The Lorentz force of the magnetic field on the moving charge carriers produces a charge separation which induces an electric field  $E_x$  perpendicular to the current and magnetic field directions. The Hall coefficient  $R_H$  is the ratio

$$R_H = E_x / JH_0 \quad (X-4)$$

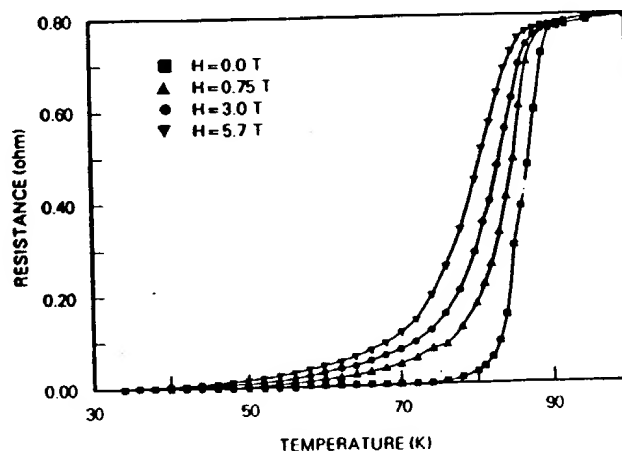


Fig. X-3. Temperature dependence of the resistance of YBaCuO in various magnetic fields from 0 to 5.7 T (Wuzzz).

Attachment B P9

where  $J$  is the current density. When the charge carriers are electrons with the density  $n$  per cubic centimeter, the Hall coefficient is negative with the value

$$R_H = -1/nec \quad (X-5)$$

in cgs units. A similar expression with a positive sign applies to hole conduction. Also of interest are the Hall mobility

$$\mu_H = R_H/\rho \quad (X-6)$$

where  $\rho$  is the resistivity, and the dimensionless Hall number  $V_0/R_{He}$ , where  $V_0$  is the volume per formula unit:

$$V_0 = 94 \text{ \AA}^3 \quad \text{for } (\text{La}_{0.925}\text{Sr}_{0.075})_2\text{CuO}_4 \quad (X-7a)$$

$$V_0 = 174 \text{ \AA}^3 \quad \text{for } \text{YBa}_2\text{Cu}_3\text{O}_7 \quad (X-7b)$$

Some authors find a strong temperature dependence of  $R_H$  or the Hall number  $V_0/R_{He}$  for  $\text{LaSrCuO}$  (Tonou) and  $\text{YBaCuO}$  (Penne, Wangz). Others find a weak dependence for  $\text{LaSrCuO}$  (Hundl, Penne, Uchi), and a large anomaly in  $R_H$  near  $T_c$  has been observed in  $\text{YBaCuO}$  (Gottw, Yongz). Figure X-4 shows  $R_H$  of three substituted  $\text{YBaCuO}$  compounds increasing strongly with decreasing temperature (Cheon, Tana1). Figure X-5 shows the temperature dependence of the Hall mobility  $\mu_H = R_H/\rho$ , the Hall number  $V_0/R_{He}$  and the resistivity  $\rho$  of an epitaxial film of  $\text{YBaCuO}$  (Chau1, Penne). Hall-effect data on various compounds are listed in Table X-3.

Hall-effect data on  $\text{LaSrCuO}$  provided the room-temperature electron concentration  $n = 1.5 \times 10^{21}/\text{cm}^3$  and the room-temperature mobility  $\mu_H = 4.17$

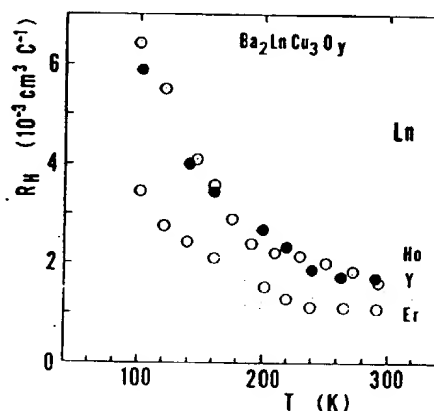


Fig. X-4. Temperature dependence of the Hall coefficient  $R_H$  of  $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$  for  $\text{Ln} = \text{Y, Ho, and Er}$  (Tana1).

Attachment B page 10

Fig.  
 $R_{He}$ .

$\text{cm}^2/\text{perat}$   
deep  
coeffi  
ially  
 $\text{cm}^3 \text{ v}$   
 $H_c$   
inhor  
Hall  
phon  
Uher.  
this c  
single  
condu  
 $H_c$   
field  
 $-0.7$   
(Toze  
band  
1-D c  
on th  
mode  
to or  
creas  
the p

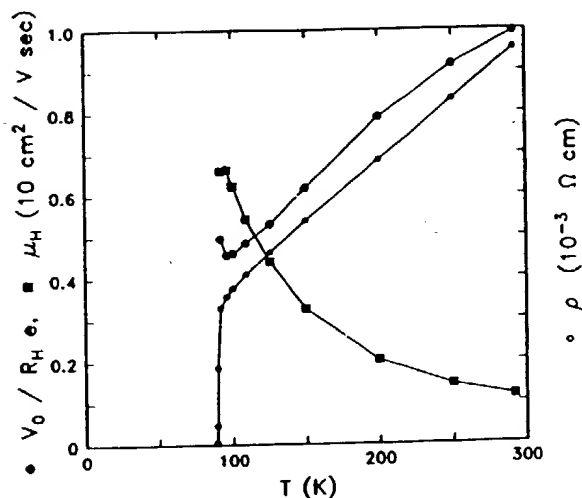


Fig. X-5. Transport data for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  showing the resistivity  $\rho$ , Hall number  $V_0/R_H$ , and Hall mobility  $\mu_H = R_H/\rho$  versus temperature (Chau1).

$\text{cm}^2/\text{V sec}$  (Tonou). The electron concentration decreases with increasing temperature, probably owing to significant capture of thermally excited electrons at deep traps in grain boundaries surrounding the conductive channels. The Hall coefficient measurement of  $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$  single-crystal films grown epitaxially on  $\text{SrTiO}_3$  provided a room-temperature carrier density  $n = 6.8 \times 10^{21}/\text{cm}^3$  which decreased notably with falling temperature (Suzuk).

Hall voltage measurements in  $\text{LaSr}^*$  indicated the presence of granular or inhomogeneous superconductivity (Hundl). The temperature dependence of the Hall coefficient of  $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_{4-\delta}$  was interpreted in terms of a relatively large phonon coupling and conduction via both electron and hole bands (Uher1, Uher3). The chemically determined electron deficiency or hole concentration in this compound exhibited a direct correlation with  $T_c$  for  $x \leq 0.15$ , suggestive of single-band transport and supportive of an all electronic mechanism for superconductivity (Shafe, Shaf1).

Hall-effect measurements on  $\text{YBa}_2\text{Cu}_3\text{O}_{8-\delta}$  single crystals with the magnetic field on  $\pm 1$  T in the  $ab$  plane yielded a negative Hall constant in the range  $-0.75$  to  $-9 \times 10^{-10} \text{ m}^3/\text{C}$  corresponding to 1.2-1.5 electrons per formula unit (Tozer). A large temperature dependence in  $R_H$  of  $\text{YBa}^*$  was attributed to multi-band conduction (Hongm) and to the temperature dependence of the 2-D and 1-D chain mobility ratio (Wangz). The Hall coefficient was inversely dependent on the temperature in the compounds  $\text{YBa}^*$  and  $\text{GdBa}^*$ , which are judged as moderately heavy Fermion-like, with a Coulomb correlation energy comparable to or larger than the bandwidths (Cheon). Around the transition a larger increase was observed in  $R_H$  for both  $\text{YBa}^*$  and  $\text{DyBa}^*$  (Yongz, Zhan1). In  $\text{DyBa}^*$  the peak in  $R_H$  corresponds to  $n \approx 4 \times 10^{19} \text{ cm}^{-3}$ , and was interpreted as a grain



TABLE X-3. Hall Effect Data<sup>a</sup>

Material	$R_H$ ( $\text{cm}^3/\text{C}$ )	$V_0/R_H^b$	$n$ ( $\text{cm}^{-3} \times 10^{21}$ )	$\mu$ ( $\text{cm}^2/\text{Vsec}$ )	$\rho$ ( $\mu\Omega \text{ cm}$ )	$T$ (K)	Ref.
LaSr*	+0.001 +0.004		6.0 2.1	4.3	600	300	Hundl
LaSr(0.1)		0.3		+0.75	2600	77	Ongzz
LaSrCuO	-0.005		1.5	-4.17	1200	300	Penne
La <sub>2</sub> CuO <sub>4</sub>	0.11		6.8	1.2	710	300	Tonou
YBa*	0.1			1.0	10 <sup>5</sup>	300	Suzuk
		1.0		+1.0	1000	300	Uchi2
		1.8		$\pm 0.5$	1300	300	Chaul
		1.4		$\pm 0.8$	950	300	Penne
	0.0005-0.002		1.4			290	Wangz

<sup>a</sup>Hall coefficient  $R_H$ , Hall number  $V_0/R_H^b$ , carrier density  $n$ , mobility  $\mu$ , resistivity  $\rho$ , and measurement temperature  $T$ . The notation used is:  $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4 = \text{LaSr}(x)$ ,  $\text{LaSr}(0.075) = \text{LaSr}$ ,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-4} = \text{YBa}$ .

<sup>b</sup>Hole concentration per formula unit.

boundary  
boundary  
with decre  
change fr  
Several  
relaxation  
holelike in  
why sign c

### 3. Therm.

A conduct  
steady-sta  
ture regio  
Seebeck el  
the superc

Figure  
Seebeck  $\alpha$   
of  $x$  (Alle  
cient decre  
compound  
was obser  
result was  
cally to a v  
activated t  
range-hop

Fig. X-6. 1  
values of  $x$

Attachment B page 12

boundary effect. In the case of  $\text{YBa}_2$ , both the intrinsic quality and the grain boundary origin were mentioned (Yongz). The Hall coefficient  $R_H$  decreases with decreasing oxygen content in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , with a plateau of very little change from  $\delta = 0.1$  to  $\delta = 0.4$  (Ongz1, Wangz).

Several papers (Allen, Alle1) have discussed the transport coefficients in the relaxation time approximation. They concluded that the Hall tensor tends to be holelike in the  $ab$  plane and electronlike in the  $ac$  and  $bc$  planes, which explains why sign differences have been reported in the literature.

### 3. Thermoelectric Effects

A conductor with a temperature gradient and no electric current develops a steady-state electrostatic potential difference between the high and low temperature regions; this phenomenon is called the thermoelectric, thermopower, or Seebeck effect. This and other related effects such as the Peltier effect vanish in the superconducting state (Hund1).

Figure X-6 shows the temperature dependence of the thermoelectric power or Seebeck coefficient  $S$  of  $\text{La}_2\text{CuO}_4$  (Gran1) and  $(\text{La}_{1-x}\text{Ba}_x)_2\text{CuO}_4$  for several values of  $x$  (Alle3, Hund1, John3, Marcu, Uchi1, Uher1, Uher2, Yanz1). The coefficient decreases with increasing  $x = 0.025, 0.05$ , and  $0.075$ , and the latter two compounds exhibit a rapid decrease to zero near the phase transition. No drop was observed in  $S$  at low temperatures for  $x = 0$ . In another study the same result was found for  $x = 0.075$ , but  $S$  for the  $x = 0$  sample decreased dramatically to a very low value below 90 K. This was attributed to a changeover from an activated type of semiconductor transport at high temperatures to a variable range-hopping type at low temperatures (Maeno).

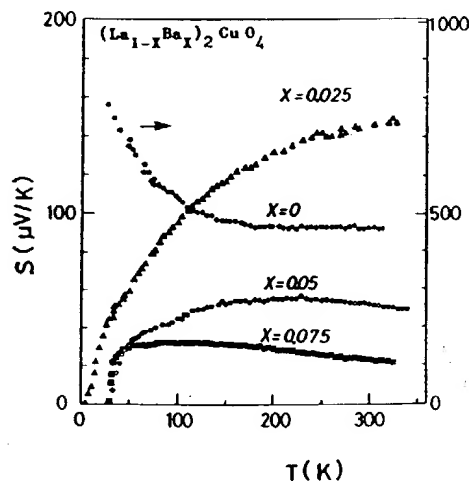


Fig. X-6. Temperature dependence of the thermopower  $S$  of  $(\text{La}_{1-x}\text{Ba}_x)_2\text{CuO}_4$  for several values of  $x$  (Uchi1).

A Hachmut B page 13

The thermopower of polycrystalline granular  $(\text{La}_{1-x}\text{M}_x)_2\text{CuO}_{4-\delta}$  with  $\text{M} = \text{Ba}$  or  $\text{Sr}$  was calculated in the effective medium approximation and the results for the  $x$  dependence of  $S(T)$  are in good agreement with experimental values (Xiazz). The room-temperature thermopower data of  $(\text{La}_{1-x}\text{M}_x)_2\text{CuO}_4$  fit the Heikes expression (Coope, Heike)

$$S = -\frac{k}{e} \left[ 2 \ln 2 + \ln \left( \frac{2x}{1-2x} \right) \right] \quad (\text{X-8})$$

where  $1 - 2x$  is the number of electrons per copper site. Note that this expression has no adjustable parameters.

There are reports that above  $T_c$  the thermopower in  $\text{YBaCuO}$  and its rare-earth-substituted analogues is positive (Mawds, Mitra), and also is negative (Khimz, Yaozh, Yuzzz), and examples of both cases are shown in Fig. X-7. An electronic or negative  $S(T)$  was observed in  $\text{O}_2$ -heated superconducting samples, and holelike behavior with positive  $S(T)$  was seen in air-heated nonsuperconducting ones (Raych). A sample of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$  exhibited a negative thermopower between 300 and 125 K attributed to a diffusion mechanism, a positive  $S(T)$  from 125 to 90 K ascribed to phonon drag effects, with  $S = 0$  below  $T_c = 90$  K (Yaozh; see also Khimz).

A large peak in the thermopower of  $\text{YBa}_4$ , called a precursor effect, was observed just above  $T_c$  (Mawds, Uher2). It was suggested that high- $T_c$  materials be used for thermopower test leads for the absolute determination of  $S(T)$  above the temperature range covered by the present standard Nb-Ti leads (Uherz).

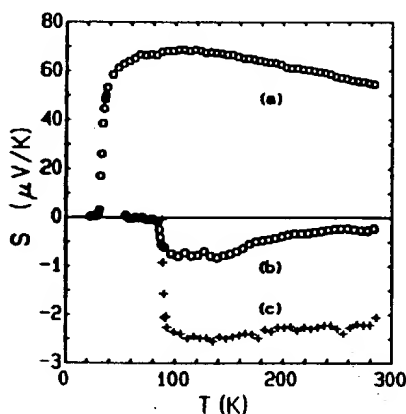


Fig. X-7. Temperature dependence of the thermopower  $S$  of (a) a ceramic sample of  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4-\delta}$ , (b) a ceramic sample of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , and (c) the  $ab$  plane of a  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  single-crystal sample. Note the different scales on the positive and negative parts of the  $y$  axis (Yuzz3).

#### 4. Photoconductivity

Photoconductivity polarons and excitivity (Masum, M

#### 5. Thermal Conductivity

The thermal conductivity is the energy that is lattice (phonons) action, mean-free thermal conductivity state. Thermal conductivity of the temperature of the temperature Fig. X-8.

A detailed study analysis of the low phonon or lattice

where

0.0

$\kappa$  ( $\text{W cm}^{-1} \text{K}^{-1}$ )

0.00

Fig. X-8. Log-log inset shows the data

Attachment B page 14

#### 4. Photoconductivity

Photoconductivity studies of LaCuO, YCuO, and YBaCuO samples suggest that polarons and excitons play a substantial role in the mechanisms of superconductivity (Masum, Masu1, Robas).

#### 5. Thermal Conductivity

The thermal conductivity  $K(T)$  is helpful in determining the fraction of the thermal energy that is transported by charge carriers and the amount carried by the lattice (phonons). It can provide information about the electron-phonon interaction, mean-free path, carrier density, and other physical properties. The thermal conductivity is not necessarily divergent or zero in the superconducting state. Thermal conductivity measurements have been reported on both polycrystalline and single-crystal samples (e.g., Bayot, More6, Uher2), and an example of the temperature dependence of  $K(T)$  in polycrystalline YBa\* is shown in Fig. X-8.

A detailed study of the transport properties of YBa\* (Gottw) included an analysis of the low-temperature ( $0.1 < T < 2$  K) behavior of  $K(T)$  in terms of a phonon or lattice contribution  $K_{ph}$  and an electronic contribution  $K_{el}$

$$K(T) = K_{ph} + K_{el} \quad (X-9)$$

where

$$K_{ph} = aT, \quad K_{el} = bT^3 \quad (X-10)$$

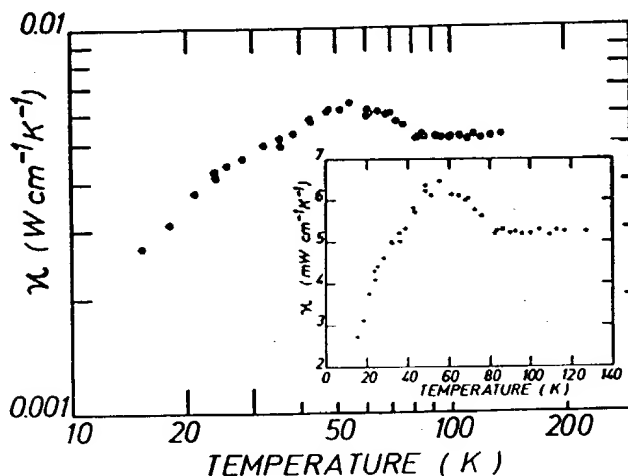


Fig. X-8. Log-log plot of the thermal conductivity of YBa\* versus the temperature. The inset shows the data replotted on a linear scale (More6).

A Hachmen + B page 15

with  $a = 16 \mu\text{W/K}^2 \text{ cm}$  and  $b = 47 \mu\text{W/K}^4 \text{ cm}$ . Hence even at  $\approx 0.1 \text{ K}$  large portions of the thermal carriers appear to be in the normal state. An observed increase in  $K(T)$  below  $T_c$  indicated large electron-phonon scattering. The authors estimated  $v_F \approx 10^7 \text{ cm/sec}$ ,  $N_{\text{eff}} \approx 10^{22}/\text{cm}^3$ , a small carrier mean-free-path, and pointed out the similarity with the heavy Fermion system  $\text{CeCu}_2\text{Si}_4$ .

There was a report that  $K_{\text{el}} < K_{\text{ph}}$  at 300 K and  $n \approx 0.13$  carriers/Cu atom (Mori6). The observed increase in  $K(T)$  below  $T_c$  may be due to freer phonon flow, and suggests that a strong electron-phonon coupling is present in  $\text{YBa}_2$ . A  $T^3$  dependence of  $K(T)$  in  $\text{YBa}_2$  below 5 K provided evidence for a temperature-independent lifetime (Herem). At 50 K the Lorentz number  $L = K\rho/T$  was estimated to be  $26 \times 10^{-8} \text{ W}\Omega/\text{K}^2$ , a factor of 20 larger than the Wiedemann-Franz value, and  $K_{\text{el}} \approx 0.1 K_{\text{ph}}$  in polycrystalline  $(\text{La}_{0.9}\text{Sr}_{0.1})_2\text{CuO}_4$  (Bartk). The thermal conductivity of sintered  $\text{YBa}_2$  in the temperature range from 0.1 to 10 K was linear in  $T$  at the lowest temperatures, and had a  $T^3$  dependence at the highest temperatures, in accordance with Eq. (X-9) (Graeb). This was claimed to be consistent with strong Rayleigh scattering of the phonons from the granular particles. In the  $ab$  plane single crystals of microtwinned  $\text{HoBa}_2$  obeyed a power law  $K(T) = aT^n$  with  $n \approx 2$ , a behavior similar to that observed in glasses (Graeb).

#### D. TUNNELING PROPERTIES

Tunneling can be carried out through an insulating layer, I, between two superconductors (S-I-S), between a superconductor and a normal material (S-I-N), and between two normal materials (N-I-N) such as two semiconductors. The dc and ac Josephson effects involve particular types of tunneling phenomena across a barrier between two superconductors. The SQUID is an application of Josephson tunneling that involves macroscopic quantum phenomena. These topics will be discussed in the following three sections.

One of the preferred ways to measure an energy gap is through tunneling experiments, and many values of the gap energy determined by this technique are recorded in Table IX-1.

##### 1. Tunneling Measurements

A tunneling study of  $\text{LaSrCuO}$  thin films was made using both the sandwich-type and the point-contact-type tunneling techniques (Naito). Sandwich-type junctions were prepared by forming a small window  $\approx 150 \mu\text{m}$  square and depositing a Pb counter electrode, which formed a natural high-resistance tunnel barrier, typically  $1 \text{ M}\Omega$ . Point contact tunneling was done with the aid of a scanning electron microscope (SEM) using a tungsten probe with a tip radius less than 100 nm. Continuous scanning was not possible, but several points on the same specimen within a  $1 \times 1 \mu\text{m}^2$  window could be sampled. The curves of differential tunneling conductances  $dI/dV$  as a function of the bias voltage presented in Fig.

X-9 have zero gap energies

In a low-temperature electrons tunneling experiments small terms of the from 3.5 to 6 grain sizes  $\leq$  study of ( $\text{Y}_0$  provided gap ratio (Ekino) tunneling current niobium tip (Gall1).

Electron tunneling differential resistance not appear in

Fig. X-9. Point contact tunneling at 4.2 K (Naito)

Attachment B page 16

X-9 have ordinate scales proportional to the density of states, and they provide gap energies.

In a low-temperature SEM tunneling study of  $(\text{La}_{0.9}\text{Sr}_{0.1})_2\text{CuO}_{4-\delta}$  at 5 K the electrons tunneled from the tip into many superconducting grains with inhomogeneities small compared to the grain sizes (Kirtl). The data were analyzed in terms of the model of Zeller and Giaever (Zelle), and gave  $E_g/kT_c$  in the range from 3.5 to 6.3. Another experiment (Tsuei) was consistent with tunneling into grain sizes  $\leq 1$  nm which are much smaller than the apparent crystal sizes. A study of  $(\text{Y}_{0.55}\text{Ba}_{0.45})_2\text{CuO}_{4-\delta}$  using point-contact tunneling at 4.2 and 27.4 K provided gap ratios  $E_g/kT_c$  in the range 3.8–4.2, somewhat larger than the BCS ratio (Ekino). Figure X-10 shows an example of the way  $I$  versus  $V$  SEM electron tunneling curves give a range of gap values ( $5 \text{ meV} \leq E_g \leq 190 \text{ meV}$ ) for a niobium tip located at various points of an aluminum-doped YBa\* sample (Gall1).

Electron tunneling between the grains of oxygen-poor YBa\* exhibited a differential resistance  $dV/dI$  which appears to have an asymptotic peak that did not appear in homogeneous oxygenated samples (Escud). The gap signature was

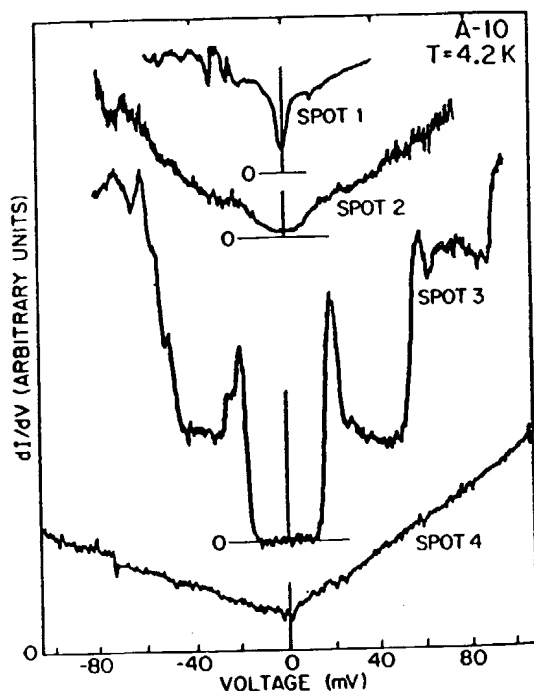


Fig. X-9. Point-contact tunneling conductance for four locations on a LaSrCuO thin film at 4.2 K (Naito).

Attachment B page 17

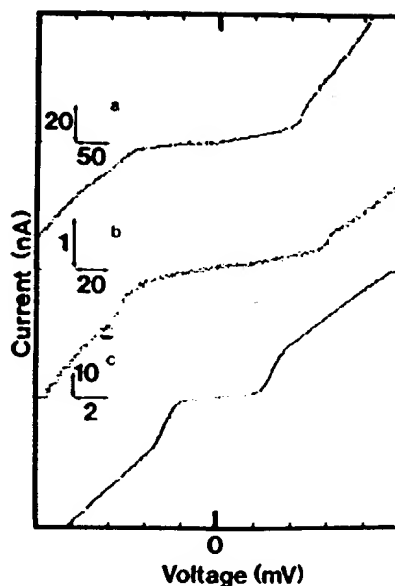


Fig. X-10. Current versus voltage plots obtained using a niobium tip at different positions on the surface of aluminum-doped  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . The difference scales used for each curve are indicated. The spectra from top to bottom show jumps in current at 95, 30, and 2.5 meV, respectively (Gall1).

not very well resolved and  $E_g/kT_c \approx 7-13$ . Tunneling studies of  $\text{YBa}^*$  thin films (Ogale) exhibited a dependence of the normalized critical current  $I_c/I_{c0}$  on  $T/T_c$ , which differs from some recent S-I-S junction calculations (Ambeg). The deGennes model was reported to be better over a small temperature range, but the predicted curvature was larger than that of the data.

In the break-junction tunneling technique (More3, More5) a small piece of bulk material is electromechanically broken under liquid helium, and the freshly fractured surfaces are adjusted to form a tunneling barrier with the liquid helium acting as the insulator (More4). The most common current-voltage curves obtained by this technique (More4) closely followed a quadratic current dependence on the voltage. Some curves have derivatives that exhibit structure indicative of the presence of gap sum voltages, and others have shapes that suggest quasi-particle tunneling between superconducting electrodes (Morel). Related behaviors are observed, for example, for tunneling from a PtIr tip into  $\text{LaSrCuO}$  (Tsuei, Zelle).

In the absence of high-quality "sandwich" junctions these break-junction results are interesting. However, the effects of the strain and elastic failure on the electronic properties of the specimens and junctions is not clear. This could be of concern, particularly in the case of ceramic superconductors that are sensitive to sample treatment.

## 2. Josephs

When two electron p  
other. The

1. The  
across the  
 $\delta$  is a phas
2. The  
 $\sin[\delta - (4$   
 $h$  is the fr
3. Mac  
with an os

where the  
magnetic  
fluxoid o

In the  
unbiased  
diatively  
Weng1).

percondu  
Anom  
field stre  
was 20 m  
above 56  
were mo:  
to flux j:  
have tra

Super  
a few mi  
could ca  
tum vol  
junction  
can pre  
voltages  
junction

Josep  
bounda

Attachment B page 18

## 2. Josephson Effect

When two superconductors are separated by a thin layer of insulating material, electron pairs can tunnel through the insulator from one superconductor to the other. There are three effects of pair tunneling, namely:

1. The dc Josephson effect, which is the flow of a dc current  $J = J_0 \sin \delta$  across the junction in the absence of an applied electric or magnetic field, where  $\delta$  is a phase factor and  $J_0$  is the maximum zero voltage current.
2. The ac Josephson effect relates to the flow of a sinusoidal current  $J = J_0 \sin[\delta - (4\pi e V t/h)]$  across a junction with an applied voltage  $V$  where  $\nu = 2eV/h$  is the frequency of oscillation.
3. Macroscopic quantum interference effects involving a tunneling current  $J$  with an oscillatory dependence on the applied field, given by

$$J = J_0 \frac{\sin \pi \Phi / \Phi_0}{\pi \Phi / \Phi_0} \quad (\text{X-11})$$

where the magnetic flux  $\Phi$  may be approximated as the product of the average magnetic field strength times the cross-sectional area, and  $\Phi_0 = hc/2e$  is the fluxoid or quantum of magnetic flux.

In the reverse ac Josephson experiment, dc voltages are induced across an unbiased junction by introducing an rf current into the junction, or by radiatively coupling an rf signal through a coil surrounding the sample (Chenz, Weng1). It was suggested that this result supports the existence of granular superconductivity in YBaCuO at 240 K (Weng1).

Anomalous voltage excursions as a function of temperature and magnetic field strength were reported above 100 K (Caizz). The onset of the excursions was 20 mT, they reached a maximum at about 33 mT, and disappeared for fields above 56 mT. The voltage jumps were different for cooling and heating, and they were more frequent for larger samples. These transient voltages were attributed to flux jumps of granular superconductors. It was proposed that some grains have transition temperatures as high as 160 K.

Superconducting oxide materials are porous with chains of grains measuring a few microns in size. Owing to the inverse Josephson effect an applied rf current could cause individual Josephson junctions in these materials to develop quantum voltages given by  $V_j = nh\nu/2e$ , which is on the order of nanovolts. Such junctions could even be inside the grains themselves (Blaze). Thermal smearing can prevent the detection of individual quantum voltages, but observable dc voltages in the millivolt range can result from the summation of thousands of junctions with  $n$  values as large as 100.

Josephson junctions in thin films of LaSr(0.1) are believed to form at grain boundaries. In one experiment the Josephson current was found to be propor-

Attachment B page 19



tional to  $[1 - (T/T_c)]^2$ . In contrast, samples of  $\text{YBa}_*$  (Cuizz) and  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  (Suzu2) produced current proportional to  $[1 - (T/T_c)]^{3/2}$ , which may suggest proximity effects (Fuku3, Kobes, Kres3, Lynto) with comparatively long-range leakage of Cooper pairs (Moriw). The proximity effect can cause two superconductors with different  $T_c$  values in contact with each other to exhibit one intermediate  $T_c$ , and it can cause a nonsuperconductor-superconductor pair to act like a superconductor with a lower  $T_c$  (Kres3).

A  $\text{LaSr}_*$  sample mounted in a point contact current-voltage probe with a conducting tip produced a hysteretic  $I$  versus  $V$  characteristic of the type shown in Fig. X-11 (Estev, Tsaiz). Microwave irradiation produced the Shapiro steps (Baron), which result from the beating of the oscillating Josephson supercurrent with the microwaves. The separation in voltage between these steps is proportional to the microwave frequency, and their amplitude is Bessel-like. The Josephson junction characteristics are observed even when the metal tip is non-superconducting, which indicates that the superconducting junction is inside the material under the tip (Estev). The absence of voltage steps during the microwave irradiation of a  $\text{Nb-YBaCuO}$  point-contact junction suggests that the coupling between the superconducting regions along the percolative path is non-Josephson (Tsaiz). Other workers studying  $\text{Nb-YBa}_*$  point-contact junctions observed Shapiro steps and an unusual noise behavior along the  $I$ - $V$  characteristic (Kuzni), and an estimate was made of  $\Delta \approx 19.5 \pm 20$  mV and  $2\Delta/kT_c \approx 4.8$  (Baro1). Very clear steps were observed in a weak link fabricated by carving a bridge ( $0.1 \times 0.2$  mm<sup>2</sup>) in a  $10 \times 2 \times 2$  mm<sup>3</sup>  $\text{YBa}_*$  sample. Both harmonic ( $n\Phi_0$ ) and subharmonic ( $n\Phi_0/m$ ) flux quantum steps were reported at 77 K (Chan2). Other microwave radiation experiments have also been carried out (McGra, Nieme, Mengz).

Theoretically microwave absorption by S-I-S junctions with square-well potentials at low temperatures is calculated to occur in sharp steps whenever the microwave energy is an integral multiple of the minimum energy needed to excite quasi particles from the ground state to bound Andreev excited states (Aberl, Andre). Andreev reflections at an  $\text{Ag-YBa}_*$  interface on a thin film have been reported. It was argued to provide evidence for Cooper or zero-momentum carrier pairs. The gap as determined from the reflection data was 12.5 meV, compared with 14 meV deduced from tunneling on the same film. These results are consistent with a BCS picture (Hoeve).

### 3. Macroscopic Quantum Phenomena

Macroscopic quantum phenomena were reported in  $\text{Sn-YBaCuO}$  and  $\text{YBaCuO-YBaCuO}$  point contacts. The critical current and the voltage are periodic in the magnetic field, and for each voltage there is a minimum and a maximum value of the current between which the oscillations take place when the magnetic field is varied (DeWae, DeWa1). This dc SQUID (Finkz, Jakle, Soule) behavior has been observed up to 40 K (Kawab), 66 K (DeWae, DeWa1), and 90 K (Tsail).

Fig. X-  
with ar  
trace. I  
(b) Ste

SQ  
The fl  
(Goug  
sampl  
operat  
 $T/\sqrt{H}$   
than t

Attachment B page 20

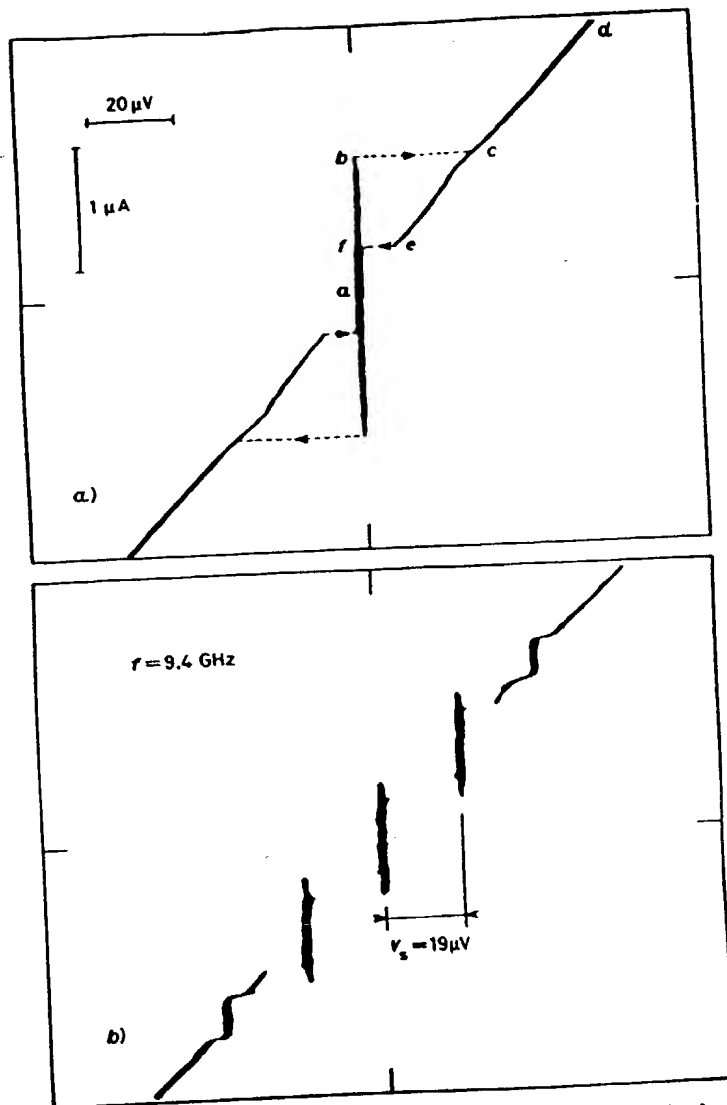


Fig. X-11. (a) Oscilloscope trace of a current-voltage characteristic obtained at 4.2 K with an aluminum tip on a  $\text{LaSr}_x$  sample. Letters a through f indicate the sense of the trace. Dashed lines have been added to indicate the switching between the two branches. (b) Steps induced by microwave irradiation at the frequency  $f = 9.4 \text{ GHz}$  (Estev).

SQUIDs have been fabricated from  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (Colcl, Kawab, Zimme). The flux quantum  $\Phi_0$  obtained from these devices was the expected  $hc/2e$  (Gough, Koch1, Koch2). For a  $\text{YBa}^*$  specimen to exhibit SQUID behavior the sample need not necessarily be multiply connected. For such a  $\text{YBa}^*$  SQUID operating in the magnetometer mode the field spectral density was  $5.8 \times 10^{-10} \text{ T}/\sqrt{\text{Hz}}$  at 4.2 K and  $1.5 \times 10^{-10} \text{ T}/\sqrt{\text{Hz}}$  at 77 K (Pegru). This value is better than that of a good flux-gate magnetometer.

Attachment B page 21

**ATTACHMENT C**

(V)

NATIONAL SCIENCE FOUNDATION  
WASHINGTON, D.C. 20550

Dear Drs. Bednorz + Müller.

12/3/86

This is just to inform you that my group  
at the U. of Houston has reproduced your  
results (Z. Phys. B 64, 189 (86)) three weeks ago.

A small ac diamagnetic signal was also  
detected. Magnetic field was found to suppress  
the transition. I believe that it is superconductivity.

Now the question is "what phase" or "mixed  
phases". Soon, you will hear from us more.

Please send me more information!

Sincerely yours

my phone:

(202) 357-9737

or

(713) 747-2842

Your phone No.?

C. W. Chui

(also Physics, Univ. of Houston)  
Houston, TX 77004

P.S. Currently, I am the Director of Solid Physics Program  
and a National Science Foundation

Attachment C



**UNITED STATES DEPARTMENT OF COMMERCE**  
**Patent and Trademark Office**

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.
-----------------	-------------	----------------------	---------------------

EXAMINER
----------

ART UNIT	PAPER NUMBER
----------	--------------

DATE MAILED:

✓ 9-12-99

Please find below and/or attached an Office communication concerning this application or proceeding.

Commissioner of Patents and Trademarks



UNITED STATES DEPARTMENT OF COMMERCE  
Patent and Trademark Office

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

SERIAL NUMBER

FILING DATE

FIRST NAMED APPLICANT

ATTORNEY DOCKET NO.

EXAMINER

ART UNIT

PAPER NUMBER

DATE MAILED:

Please find below a communication from the EXAMINER in charge of the application.

Commissioner of Patents.

**NOTIFICATION OF NON-COMPLIANCE WITH THE REQUIREMENTS OF 37 CFR 1.192(c)**

The brief does not contain a statement of the status of an amendment filed subsequent to the final rejection as required by 37 CFR 1.192(c)(4).

At pages 4 of the Brief, Appellant specifies ten after-final submissions: November 25, 1998; December 10, 1998; December 11, 1998; December 14, 1998; December 15, 1998 (3 submissions); December 18, 1998; December 22, 1998; and December 27, 1998. Page 5 of the Brief specifies four additional submissions: June 14, 1999; June 15, 1999 (2 submissions); and June 24, 1999 (the June 24, 1999 paper being a resubmission of the December 27, 1998 paper).

The amendment filed **December 14, 1998** has **not** been received or reviewed by the examiner. The status and content of the amendment is unknown. Correction is required.

Below is a listing of the status of the remaining submissions:

November 25, 1998: Not entered (Advisory mailed 12/14/98 (Paper #68))

December 10, 1998: Not entered (Advisory mailed 2/25/99 (Paper 77C))

December 11, 1998: Not entered (Advisory mailed 2/25/99 (Paper 77A))

December 15, 1998: [1.132 Declarations of Mitzi, Tsuei, Dinger and Shaw]

Entered (Advisory mailed 2/25/99 (Paper 77E))

December 15, 1998: [1.132 Declaration of James Leonard] Not entered (Advisory

mailed 2/25/99 (Paper 77B))

December 18, 1998: Entered (Advisory mailed 2/25/99 (Paper 77E))

December 22, 1998: Not entered (Advisory mailed 2/25/99 (Paper 77A))

December 27, 1998: Not entered (Advisory mailed 2/25/99 (Paper 77D))

June 14, 1999: Entered (Advisory mailed 7/8/99 (Paper #83))

June 15, 1999 (2): Entered (Advisory Actions mailed 7/8/99 (Paper #84 and 85))

June 27, 1999: Not Entered (Advisory mailed 7/8/99 (Paper #86))

Also, the brief does not contain the items of the brief required by 37 CFR 1.192(c) under the appropriate headings and/or in the order indicated. Specifically, the "Summary of the Invention" should precede both the "Issues" and "Grouping of Claims" sections. Correction is required.

Appellant is required to comply with provisions of 37 CFR 1.192(c).

To avoid dismissal of the appeal, Appellant must comply with the provisions of 37 CFR 1.192(c) within the longest of any of the following TIME PERIODS: (1) ONE MONTH or THIRTY DAYS, whichever is longer, from the mailing of this communication; (2) within the time period for reply to the action from which appeal has been taken; or (3) within two months from the date of the notice of appeal under 37 CFR 1.191. Extensions of these time periods may be granted under 37 CFR 1.136.


Any inquiry concerning this communication or earlier communications from the examiner should be directed to Mark Kopec whose telephone number is (703) 308-1088. The examiner can normally be reached on Monday-Thursday from 7:30 AM - 6:00 PM.

If reasonable attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Dr. Yogendra Gupta, can be reached on (703) 308-4708.

The official fax phone numbers for this Group are (703) 305-7718 and 305-3599 (for after-final submissions).

Any inquiry of a general nature or relating to the status of this application should be directed to the Group receptionist whose telephone number is (703) 308-0661.

Mark Kopec  
September 12, 1999

  
Mark Kopec  
Primary Examiner

OO-IBM YORKTOWN

DATE	TIME	TO/FROM	MODE	MIN/SEC	PGS	CMD#	STATUS
08	09/02 11:33	7033057718	EC--S	01'01"	004	009	OK

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Date: September 2, 1999

Applicants: Bednorz et al.

Group Art Unit: 1751

Serial No.: 08/303,561

Examiner: M. Kopec

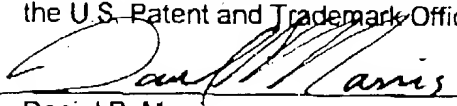
Filed: September 9, 1994

Docket No: YO987-0748Y

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURES, METHODS FOR THEIR USE AND PREPARATION

Assistant Commissioner for Patents  
Washington, D. C. 20231

I hereby certify that this paper is being facsimile transmitted under Rule CFR 1.61(d) to  
the U.S. Patent and Trademark Office to (703) 305-7718 on the date shown above.

  
Daniel P. Morris  
Reg. No. 32,053

**SUPPLEMENTARY APPEAL BRIEF**

**Supplementary Argument To Claim Rejections Under 35 USC 112, First Paragraph**

The CCPA held in In re Grice 133 USPQ 365 (1962) in regard to plant patents  
(and followed this In re Sasse, Beck and Eue, 207 USPQ 107 (1980), in regard to utility  
patents that:

the proper test of a description in the publication as a bar to a patent as  
the clause is used in section 102(b) requires a determination of whether



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Date: September 2, 1999

Applicants: Bednorz et al.

Group Art Unit: 1751

Serial No.: 08/303,561

Examiner: M. Kopec

Filed: September 9, 1994

Docket No: YO987-074BY

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURES, METHODS FOR THEIR USE AND PREPARATION

Assistant Commissioner for Patents  
Washington, D. C. 20231

I hereby certify that this paper is being facsimile transmitted under Rule CFR 1.61(d) to  
the U.S. Patent and Trademark Office to (703) 305-7718 on the date shown above.



Daniel P. Morris  
Reg. No. 32,053

**SUPPLEMENTARY APPEAL BRIEF**

**Supplementary Argument To Claim Rejections Under 35 USC 112, First Paragraph**

The CCPA held in In re Grice 133 USPQ 365 (1962) in regard to plant patents  
(and followed this In re Sasse, Beck and Eue, 207 USPQ 107 (1980), in regard to utility  
patents that:

the proper test of a description in the publication as a bar to a patent as  
the clause is used in section 102(b) requires a determination of whether

one skilled in the art to which the invention pertains could take the description of the invention in the printed publication and combine it with his own knowledge of the particular art and from this combination *be put in possession of the invention on which a patent is sought*. Unless this condition prevails, the description in the printed publication is inadequate as a statutory bar to patentability under section 102(b). [Emphasis added in *In re Sasse, Beck and Eue*.]

Since the same language is used in Section 102(a), the same test applies. In *re Sheppard*, 144 USPQ 42 (CCPA 1964); *Kenmode v. United States*, 145 USPQ 658 (CCPA 1965); and *DuPont v Ladd*, 140 USPQ 297 (DC Cir. 1964). Therefore, the Examiner's rejection of all of Applicants' claims, except for claim 136, under Section 102(a) necessarily means that the Examiner believes that a person of skill in the art is put in possession of applicants claimed invention by the *Asahi Shinbum* article which refers to Applicants' work and reports the reproduction of Applicants' work in Japan based on Applicants' teaching as described in detail in the Brief. Thus, it is the Examiner's view that all of Applicant's claims are enabled by Applicants' teaching.

In *In re Marzocchi*, 169 USPQ 367, 370 (1971) the CCPA has said:

In any event, it is incumbent upon the Patent Office, whenever a rejection on this basis is made [35 USC 112, paragraph 1, enablement], to explain *why* it doubts the truth or accuracy of any statement in a supporting disclosure and to back up assertions of its own with acceptable evidence or reasoning which is inconsistent with the contested statement.

The Examiner has merely stated without extrinsic evidence that the art of high  $T_c$  superconductivity is unpredictable. The Examiner points to examples on applicants' specification which do not show high  $T_c$  superconductivity which as stated in detail in the Brief are part of Applicants' enabling disclosure.

In In re Wright, 27 USPQ2d 1510, 1513, the CAFC has said:

Although not explicitly stated in section 112, to be enabling, the specification of a patent must teach those skilled in the art how to make and use the full scope of the claimed invention without "undue experimentation".

The Examiner has presented no evidence to indicate that "undue experimentation" is required to practice the inventions of Applicants' claims rejected under 35 USC 112, first paragraph. To the contrary, Applicants have submitted substantial evidence showing the processes to make the compositions which are high  $T_c$  superconductors were well known prior to applicants filing date and easily practiced. Applicants discovery is that these materials are high  $T_c$  superconductors. Thus no "undue experimentation" is necessary to practice Applicants claimed invention. Consequently, the section 112, first paragraph rejections is not only inconsistent with the section 102(a) rejections but is also unfounded and should be reversed.

A patent application is not intended on being a blue print, Staechelin v. Secher 24 USPQ2d 1513, 1516 (BPAI 1992), some experimentation is permitted, Bruning v. Hirose 48 USPQ2d 1934, 1939 (CAFC 1998). "Not every last detail is to be described, else patent specifications would turn into production specifications which they were never intended to be", In re Gay 135 USPQ 316 (CCPA 1962). It is a matter of routine experimentation, based on Applicants' teaching to determine specific examples, other than those specifically described in Applicants' specification, which are within the scope of Applicants' claims.

The Constitutional Policy of the US Patent System is to promote the progress of the useful arts by inducing early disclosure of inventions which Applicants have done by the publication for which they receive the Nobel Prize in 1987. The Examiner's

inconsistent arguments frustrate this policy and the purpose the US Patent Law.  
The Board is requested to reverse the rejection of Applicants' claims under 35 USC  
112, first paragraph.

Respectfully submitted,

By:



Daniel P. Morris

Reg. No. 32,053

Telephone No.: (914) 945-3217

IBM Corporation  
Intellectual Property Law Dept.  
P. O. Box 218  
Yorktown Heights, New York 10598

00-IBM YORKTOWN

	DATE	TIME	TO/FROM	MODE	MIN/SEC	PGS	CMD#	STATUS
05	09/01	16:52	7033057718	EC--S	01'27"	000	007	INC
07	09/01	16:54	7033057718	EC--S	00'30"	002	007	OK

---

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/303,561

Filed: September 9, 1994

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURES, METHODS FOR THEIR USE AND PREPARATION

Date: September 1, 1999

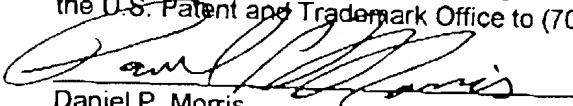
Group Art Unit: 1751

Examiner: M. Kopec

Docket No: YO987-074BY

Assistant Commissioner for Patents  
Washington, D. C. 20231

I hereby certify that this paper is being facsimile transmitted under Rule CFR 1.61(d) to  
the U.S. Patent and Trademark Office to (703) 305-7718 on the date shown above.

  
Daniel P. Morris  
Reg. No. 32,053AMENDMENT TO APPEAL BRIEF

At page 5, line 1 of issue 4,

delete "and"; replace therefor --,--

after "139-142" add --, 143-163, 164-166, 169, 170 and 174-177--.

At page 5, line 1 of issue 5,

delete "and"; replace therefor --,--

after "137-142" add --, 164-169 and 170-177--.

At page 102, line 2, delete "139-177"; replace therefor --135-166, 169, 170 and  
174-177--.At page 115, line 2, delete "and"; replace therefor --,--; after "137-142" add --164-169  
and 170-177--.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/303,561

Filed: September 9, 1994

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURES, METHODS FOR THEIR USE AND PREPARATION

Date: September 1, 1999

Group Art Unit: 1751

Examiner: M. Kopec

Docket No: YO987-074BY

Assistant Commissioner for Patents  
Washington, D. C. 20231

I hereby certify that this paper is being facsimile transmitted under Rule CFR 1.61(d) to  
the U.S. Patent and Trademark Office to (703) 305-7718 on the date shown above.



Daniel P. Morris  
Reg. No. 32,053

**AMENDMENT TO APPEAL BRIEF**

At page 5, line 1 of issue 4,

delete "and"; replace therefor --,--

after "139-142" add --, 143-163, 164-166, 169, 170 and 174-177--.

At page 5, line 1 of issue 5,

delete "and"; replace therefor --,--

after "137-142" add --, 164-169 and 170-177--.

At page 102, line 2, delete "139-177"; replace therefor --135-166, 169, 170 and  
174-177--.

At page 115, line 2, delete "and"; replace therefor --,--; after "137-142" add --164-169  
and 170-177--.

At page 58, 2 lines from the bottom, delete "Sn<sup>2x</sup>"; replace therefor --Sn<sub>2x</sub>--.

At page 58, last line, delete "Ba<sup>2x</sup> and Ca<sup>2x</sup>"; replace therefor --Ba<sub>2x</sub> and Ca<sub>2x</sub>--.

At page 69, line 8, delete "enclosed herewith"; replace therefor --submitted--.

At page 69, 4 lines from the bottom, delete "ee@@".

At page 80, line 4, delete "1:1"; replace therefor --1:1--.

At page 86, 3 lines from the bottom, delete "below" replace therefor --above--.

At page 91, 5 lines from the bottom, delete "enabling"; replace therefor --enabled--.

#### REMARKS

Typographical errors have been corrected.

Respectfully submitted,

By: 

Daniel P. Morris

Reg. No. 32,053

Telephone No.: (914) 945-3217

IBM Corporation  
Intellectual Property Law Dept.  
P. O. Box 218  
Yorktown Heights, New York 10598



UNITED STATES DEPARTMENT OF COMMERCE  
Patent and Trademark Office

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.
08/303,561	09/09/94	BELNORZ	I Y0987074BY

DANIEL P. MORRIS  
IBM CORPORATION  
INTELLECTUAL PROPERTY LAW DEPARTMENT  
P O BOX 218  
YORKTOWN HEIGHTS NY 10598

1M62/0708

EXAMINER	
KOPEC, M	
ART UNIT	PAPER NUMBER
1751	86

DATE MAILED:

07/08/99

Below is a communication from the EXAMINER in charge of this application

COMMISSIONER OF PATENTS AND TRADEMARKS

ADVISORY ACTION

☒ THE PERIOD FOR RESPONSE:

☒ is extended to run 1 year from the date of the Final Rejection

☐ continues to run \_\_\_\_\_ from the date of the Final Rejection

☐ expires three months from the date of the final rejection or as of the mailing date of this Advisory Action, whichever is later. In no event however, will the statutory period for response expire later than six months from the date of the final rejection.

Any extension of time must be obtained by filing a petition under 37 CFR 1.136(a), the proposed response and the appropriate fee. The date on which the response, the petition, and the fee have been filed is the date of the response and also the date for the purposes of determining the period of extension and the corresponding amount of the fee. Any extension fee pursuant to 37 CFR 1.17 will be calculated from the date that the shortened statutory period for response expires as set forth above.

☒ Appellant's Brief is due in accordance with 37 CFR 1.192(a).

☒ Applicant's response to the final rejection, filed 5/24/98, has been considered with the following affect, but it is not deemed to place the application in condition for allowance: (Petition to 37 CFR 1.102, filed 12/27/98)

1. ☐ The proposed amendments to the claim and/or specification will not be entered and the final rejection stands because:

- ☐ There is no convincing showing under 37 CFR 1.116(b) why the proposed amendment is necessary and was not earlier presented.
- ☐ They raise new issues that would require further consideration and/or search. (See Note).
- ☐ They raise the issue of new matter. (See Note).
- ☐ They are not deemed to place the application in better form for appeal by materially reducing or simplifying the issues for appeal.
- ☐ They present additional claims without cancelling a corresponding number of finally rejected claims.

NOTE:

The language "typical" is not allowable for the reasons stated in the attached letter. The language "typical" is not allowable for the reasons stated in the attached letter. The language "typical" is not allowable for the reasons stated in the attached letter.

2. ☐ Newly proposed or amended claims \_\_\_\_\_ would be allowed if submitted in a separately filed amendment cancelling the non-allowable claims.

3. ☐ Upon the filing of an appeal, the proposed amendment ☐ will be ☐ will not be, entered and the status of the claims in this application would be as follows:

Allowed claims: \_\_\_\_\_

Claims objected to: \_\_\_\_\_

Claims rejected: \_\_\_\_\_

However;

a. ☐ The rejection of claims \_\_\_\_\_ on references is deemed to be overcome by applicant's response.

b. ☐ The rejection of claims \_\_\_\_\_ on non-reference grounds only is deemed to be overcome by applicant's response.

4. ☐ The affidavit, exhibit or request for reconsideration has been considered but does not overcome the rejection.

5. ☒ The affidavit or exhibit will not be considered because applicant has not shown good and sufficient reasons why it was not earlier presented. SEE NOTE.

☐ The proposed drawing correction ☐ has ☐ has not been approved by the examiner.

☐ Other

Mark Kopec  
Mark Kopec  
Primary Examiner





UNITED STATES DEPARTMENT OF COMMERCE  
Patent and Trademark Office

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.
08/303,561	09/09/94	REDMOND	Y00070741Y

DANIEL P. MORRIS  
IBM CORPORATION  
INTELLECTUAL PROPERTY LAW DEPARTMENT  
P O BOX 218  
YORKTOWN HEIGHTS NY 10598

IM62/0702

EXAMINER	
ART UNIT	PAPER NUMBER
1741	85

DATE MAILED:

Below is a communication from the EXAMINER in charge of this application  
COMMISSIONER OF PATENTS AND TRADEMARKS

07/08/99

ADVISORY ACTION

☒ THE PERIOD FOR RESPONSE:

- ☒ is extended to run 6 months from the date of the Final Rejection
- ☐ continues to run \_\_\_\_\_ from the date of the Final Rejection
- ☐ expires three months from the date of the final rejection or as of the mailing date of this Advisory Action, whichever is later. In no event however, will the statutory period for response expire later than six months from the date of the final rejection.

Any extension of time must be obtained by filing a petition under 37 CFR 1.136(a), the proposed response and the appropriate fee. The date on which the response, the petition, and the fee have been filed is the date of the response and also the date for the purposes of determining the period of extension and the corresponding amount of the fee. Any extension fee pursuant to 37 CFR 1.17 will be calculated from the date that the shortened statutory period for response expires as set forth above.

☒ Appellant's Brief is due in accordance with 37 CFR 1.192(a).

☒ Applicant's response to the final rejection, filed 4/15/99, has been considered with the following affect, but it is not deemed to place the application in condition for allowance: (8, p. 40)

1. ☐ The proposed amendments to the claim and/or specification will not be entered and the final rejection stands because:
- ☐ There is no convincing showing under 37 CFR 1.116(b) why the proposed amendment is necessary and was not earlier presented.
  - ☐ They raise new issues that would require further consideration and/or search. (See Note).
  - ☐ They raise the issue of new matter. (See Note).
  - ☐ They are not deemed to place the application in better form for appeal by materially reducing or simplifying the issues for appeal.
  - ☐ They present additional claims without cancelling a corresponding number of finally rejected claims.

NOTE: \_\_\_\_\_

2. ☐ Newly proposed or amended claims \_\_\_\_\_ would be allowed if submitted in a separately filed amendment cancelling the non-allowable claims.

3. ☒ Upon the filing of an appeal, the proposed amendment ☒ will be ☐ will not be, entered and the status of the claims in this application would be as follows:

Allowed claims: 1-6

Claims objected to: \_\_\_\_\_

Claims rejected: 7-10, 11-16, 17-19

However:

- ☐ The rejection of claims \_\_\_\_\_ on references is deemed to be overcome by applicant's response.
  - ☐ The rejection of claims \_\_\_\_\_ on non-reference grounds only is deemed to be overcome by applicant's response.
4. ☒ The affidavit, exhibit or request for reconsideration has been considered but does not overcome the rejection. SEE ATTACH.
5. ☐ The affidavit or exhibit will not be considered because applicant has not shown good and sufficient reasons why it was not earlier presented.

- ☐ The proposed drawing correction ☐ has ☐ has not been approved by the examiner.
- ☐ Other



UNITED STATES DEPARTMENT OF COMMERCE  
Patent and Trademark Office

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.
08/303,561	09/09/94	BEDNORZ	J Y0987074B

DANIEL P. MORRIS  
IBM CORPORATION  
INTELLECTUAL PROPERTY LAW DEPARTMENT  
P.O. BOX 218  
YORKTOWN HEIGHTS NY 10598

1M62/0708

EXAMINER	
KOPEC M	
ART UNIT	PAPER NUMBER
1751	84

DATE MAILED:

07/08/99

Below is a communication from the EXAMINER in charge of this application

COMMISSIONER OF PATENTS AND TRADEMARKS

ADVISORY ACTION

☒ THE PERIOD FOR RESPONSE:

- ☒ is extended to run 6 mos from the date of the Final Rejection
- ☐ continues to run \_\_\_\_\_ from the date of the Final Rejection
- ☐ expires three months from the date of the final rejection or as of the mailing date of this Advisory Action, whichever is later. In no event however, will the statutory period for response expire later than six months from the date of the final rejection.

Any extension of time must be obtained by filing a petition under 37 CFR 1.136(a), the proposed response and the appropriate fee. The date on which the response, the petition, and the fee have been filed is the date of the response and also the date for the purposes of determining the period of extension and the corresponding amount of the fee. Any extension fee pursuant to 37 CFR 1.17 will be calculated from the date that the shortened statutory period for response expires as set forth above.

☒ Appellant's Brief is due in accordance with 37 CFR 1.192(a).

☒ Applicant's response to the final rejection, filed 6/5/99 (Paper #19) has been considered with the following affect, but it is not deemed to place the application in condition for allowance:

1. ☐ The proposed amendments to the claim and/or specification will not be entered and the final rejection stands because:
- ☐ There is no convincing showing under 37 CFR 1.116(b) why the proposed amendment is necessary and was not earlier presented.
  - ☐ They raise new issues that would require further consideration and/or search. (See Note).
  - ☐ They raise the issue of new matter. (See Note).
  - ☐ They are not deemed to place the application in better form for appeal by materially reducing or simplifying the issues for appeal.
  - ☐ They present additional claims without cancelling a corresponding number of finally rejected claims.

NOTE:

2. ☐ Newly proposed or amended claims \_\_\_\_\_ would be allowed if submitted in a separately filed amendment cancelling the non-allowable claims.

3. ☒ Upon the filing of an appeal, the proposed amendment ☒ will be ☐ will not be, entered and the status of the claims in this application would be as follows:

Allowed claims: 136

Claims objected to: \_\_\_\_\_

Claims rejected: 24-26, 81-10, 11-15, 127-163

However:

- ☐ The rejection of claims \_\_\_\_\_ on references is deemed to be overcome by applicant's response.
- ☐ The rejection of claims \_\_\_\_\_ on non-reference grounds only is deemed to be overcome by applicant's response.

4. ☒ The affidavit, exhibit or request for reconsideration has been considered but does not overcome the rejection. SEE ATTACH

5. ☐ The affidavit or exhibit will not be considered because applicant has not shown good and sufficient reasons why it was not earlier presented.

- ☐ The proposed drawing correction ☐ has ☐ has not been approved by the examiner.

- ☐ Other

*Mark Kopec*  
Mark Kopec  
Primary Examiner



UNITED STATES DEPARTMENT OF COMMERCE  
Patent and Trademark Office

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.
08/303,561	09/09/94	BEINORZ	Y0987074BY

DANIEL P. MORRIS  
IBM CORPORATION  
INTELLECTUAL PROPERTY LAW DEPARTMENT  
P.O. BOX 213  
YORKTOWN HEIGHTS NY 10598

IM62/0708

EXAMINER	
SUPERVISOR	
ART UNIT	PAPER NUMBER
1751	83

DATE MAILED:

07/08/99

Below is a communication from the EXAMINER in charge of this application  
COMMISSIONER OF PATENTS AND TRADEMARKS

ADVISORY ACTION

☒ THE PERIOD FOR RESPONSE:

- ☒ is extended to run 6 mos from the date of the Final Rejection
- ☐ continues to run \_\_\_\_\_ from the date of the Final Rejection
- ☐ expires three months from the date of the final rejection or as of the mailing date of this Advisory Action, whichever is later. In no event however, will the statutory period for response expire later than six months from the date of the final rejection.

Any extension of time must be obtained by filing a petition under 37 CFR 1.136(a), the proposed response and the appropriate fee. The date on which the response, the petition, and the fee have been filed is the date of the response and also the date for the purposes of determining the period of extension and the corresponding amount of the fee. Any extension fee pursuant to 37 CFR 1.17 will be calculated from the date that the shortened statutory period for response expires as set forth above.

- ☒ Appellant's Brief is due in accordance with 37 CFR 1.192(a).
- ☒ Applicant's response to the final rejection, filed 6/14/99, has been considered with the following affect, but it is not deemed to place the application in condition for allowance: (Paper #78)

1. ☐ The proposed amendments to the claim and/or specification will not be entered and the final rejection stands because:
- ☐ There is no convincing showing under 37 CFR 1.116(b) why the proposed amendment is necessary and was not earlier presented.
  - ☐ They raise new issues that would require further consideration and/or search. (See Note).
  - ☐ They raise the issue of new matter. (See Note).
  - ☐ They are not deemed to place the application in better form for appeal by materially reducing or simplifying the issues for appeal.
  - ☐ They present additional claims without cancelling a corresponding number of finally rejected claims.

NOTE: The amendment has overcome the 112, 2nd IP, rejections. These claims exist for the rejections directed to the terms "pyrosilicate-like" and "fiber-type" in the 112, 2nd IP, rejection of claims 131, 135, 137-142 is withdrawn (page 12 of Paper #66)

2. ☐ Newly proposed or amended claims \_\_\_\_\_ would be allowed if submitted in a separately filed amendment cancelling the non-allowable claims.
3. ☒ Upon the filing of an appeal, the proposed amendment ☒ will be ☐ will not be, entered and the status of the claims in this application would be as follows:

Allowed claims: 136

Claims objected to: \_\_\_\_\_

Claims rejected: 24-26, 86-90, 96-135, 137-142

However:

- ☐ The rejection of claims \_\_\_\_\_ on references is deemed to be overcome by applicant's response.
  - ☒ The rejection of claims 135, 137, 138 on non-reference grounds only is deemed to be overcome by applicant's response.
4. ☐ The affidavit, exhibit or request for reconsideration has been considered but does not overcome the rejection.
5. ☐ The affidavit or exhibit will not be considered because applicant has not shown good and sufficient reasons why it was not earlier presented.
- ☐ The proposed drawing correction ☐ has ☐ has not been approved by the examiner.
- ☐ Other

Mark Kopec  
Primary Examiner

Application/Control Number: 08/303,561

Page 2  
(Paper #84)

Art Unit: 1751

Applicant's remarks appearing at page 13 of the response are noted. Specifically, the newly added claims do **not** add any new issues and therefore would **not** cause a withdrawal of the final rejection.

Upon appeal, claims **143-163** will be added to the **112, first paragraph, rejection** set forth at page 6 of Paper #66 (Final Rejection) and the **102(a) rejection** over Asahi Shinbum article set forth at pages 16-19 of Paper #66 (Final Rejection).


Any inquiry concerning this communication or earlier communications from the examiner should be directed to Mark Kopec whose telephone number is (703) 308-1088. The examiner can normally be reached on Monday-Thursday from 7:30 AM - 6:00 PM.

If reasonable attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Dr. Yogendra Gupta, can be reached on (703) 308-4708.

The official fax phone numbers for this Group are (703) 305-7718 and 305-3599 (for after-final submissions).

Any inquiry of a general nature or relating to the status of this application should be directed to the Group receptionist whose telephone number is (703) 308-0661.

Mark Kopec  
July 7, 1999

  
Mark Kopec  
Primary Examiner

Application/Control Number: 08/303,561

Page 2

Art Unit: 1751

(Paper #85)

Applicant's remarks appearing at page 5 of the response are noted. Specifically, the newly added claims do **not** add any new issues and therefore would **not** cause a withdrawal of the final rejection.

Upon appeal, claims **143-163** will be added to the **112, first paragraph, rejection** set forth at page 6 of Paper #66 (Final Rejection) and the **102(a) rejection** over Asahi Shinbum article set forth at pages 16-19 of Paper #66 (Final Rejection).


Any inquiry concerning this communication or earlier communications from the examiner should be directed to Mark Kopec whose telephone number is (703) 308-1088. The examiner can normally be reached on Monday-Thursday from 7:30 AM - 6:00 PM.

If reasonable attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Dr. Yogendra Gupta, can be reached on (703) 308-4708.

The official fax phone numbers for this Group are (703) 305-7718 and 305-3599 (for after-final submissions).

Any inquiry of a general nature or relating to the status of this application should be directed to the Group receptionist whose telephone number is (703) 308-0661.

Mark Kopec  
July 7, 1999

  
Mark Kopec  
Primary Examiner

FILING TRANSMITTAL FEE FOR FILING AN APPEAL BRIEF, APPEAL TO  
THE BOARD OF APPEALS (3 Sets), REQUEST FOR ORAL HEARING, AND  
CERTIFICATE OF MAILING. *Amendment After Final Rejection*

DATE OF DEPOSIT: JUNE 28, 1999

PLEASE STAMP & RETURN TO US

in re application of: J. Bednorz et al.

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION ...

Serial No.: 08/303,561; Docket No.: Y0987-074BY Atty.: DPM

Received in the U.S. Patent & Trademark Office: \_\_\_\_\_

No. of pages of specification: \_\_\_\_\_; No. of pages of claims: \_\_\_\_\_

No. of sheets of drawings: \_\_\_\_\_

Declaration is attached to specification.

All fees are charged to our Account No. 09-0468

FILING TRANSMITTAL FEE FOR FILING AN APPEAL BRIEF, APPEAL TO  
THE BOARD OF APPEALS (3 Sets), REQUEST FOR ORAL HEARING, AND  
CERTIFICATE OF MAILING. *Amendment After Final Rejection*

DATE OF DEPOSIT: JUNE 28, 1999

PLEASE STAMP & RETURN TO US

in re application of: J. Bednorz et al.

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION ...

Serial No.: 08/303,561; Docket No.: Y0987-074BY Atty.: DPM

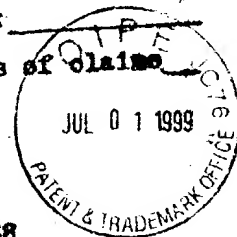
Received in the U.S. Patent & Trademark Office: \_\_\_\_\_

No. of pages of specification: \_\_\_\_\_; No. of pages of claims: \_\_\_\_\_

No. of sheets of drawings: \_\_\_\_\_

Declaration is attached to specification.

All fees are charged to our Account No. 09-0468



**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of: J. Bednorz et al.

Docket No.: YO987-074BY

Serial No: 08/303,561

Group Art Unit: 1751

Filed: 09/09/94

Examiner: D. McGinty

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

Assistant Commissioner for Patents  
Washington, D.C. 20231

**CERTIFICATE OF MAILING UNDER 37 CFR 1.8 (a)**

I hereby certify that the attached correspondence comprising:

Transmittal Fee for Filing an Appeal Brief  
Appeal to the Board of Appeals (3 sets)  
Request for Oral Hearing  
Acknowledgment Card  
*Amendment After Final Rejection*

is being deposited with the United States Postal Service as first class mail in an envelope addressed to:

**Assistant Commissioner for Patents  
Washington, D.C. 20231**

on June 28, 1999

Daniel P. Morris

(Type or printed name of person mailing paper or fee)



(Signature of person mailing paper or fee)

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of: J. Bednorz et al.

Date: June 28, 1999

Serial No: 08/303,561

Group Art Unit: 1751

Filed: 09/09/94

Examiner: D. McGinty

For: NEW SUPERCONDUCTIVE COMPOUNDS  
HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION

Docket No.: YO987-074BY

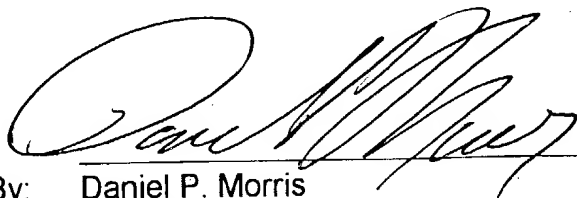
Assistant Commissioner for Patents  
Washington, D.C. 20231

**TRANSMITTAL FEE FOR FILING AN APPEAL BRIEF**

Sir:

Enclosed herewith is Applicants' appeal brief in triplicate. Please charge deposit account no. 09-0468 the fee of \$300.00 under 37 CFR 1.17(f) and any other fee necessary to enter this appeal brief.

Respectfully submitted,

  
By: Daniel P. Morris  
Registration No.: 32,053  
Phone Number: 914-945-3217

IBM Corporation  
Intellectual Property Law Department  
P.O. Box 218  
Yorktown Heights, New York 10598



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of: J. Bednorz et al.

Date: June 28, 1999

Serial No: 08/303,561

Group Art Unit: 1751

Filed: 09/09/94

Examiner: D. McGinty

For: NEW SUPERCONDUCTIVE COMPOUNDS  
HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION

Docket No.: YO987-074BY

Assistant Commissioner for Patents  
Washington, D.C. 20231

REQUEST FOR ORAL HEARING

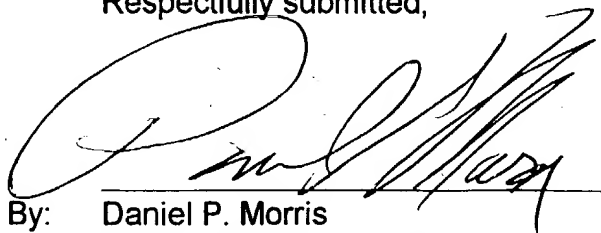
Sir:

Applicants' request an oral hearing in the appeal of the above-identified application.

Due to the number and complexity of the issues on appeal, Applicants request an extended oral hearing. Applicants' request at least one (1) hour.

Please charge deposit account no. 09-0468 the fee under 37 CFR 1.17(g) and any other fee necessary to enter this request.

Respectfully submitted,



By: Daniel P. Morris  
Registration No.: 32,053  
Phone Number: 914-945-3217

IBM Corporation  
Intellectual Property Law Department  
P.O. Box 218  
Yorktown Heights, New York 10598

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/303,561

Filed: 09/09/94

Date: June 28, 1999

Group Art Unit: 1751

Examiner: M. Kopec

For: New Superconductive Compounds Having High Transition  
Temperatures, Methods For Their Use and Preparation

Assistant Commissioner for Patents  
Washington, D. C. 20231

In response to the final rejection dated June 25, 1998 please consider the following:

**IN THE CLAIMS**

In Claims 110 and 125, line 2, delete "any" replace therefor --an--.

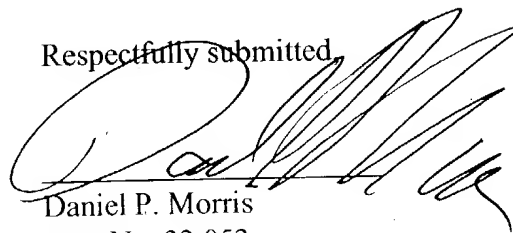
In Claim 153 delete "103"; replace therefor -- 152 --.

**REMARKS**

Typographical errors are corrected in the claims.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

Respectfully submitted,



Daniel P. Morris  
Reg. No. 32,053  
(914) 945-3217

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/303,561

Filed: 09/09/94

Date: June 28, 1999

Group Art Unit: 1751

Examiner: M. Kopec

For: New Superconductive Compounds Having High Transition  
Temperatures, Methods For Their Use and Preparation

Assistant Commissioner for Patents  
Washington, D. C. 20231

**APPEAL TO THE BOARD OF APPEALS AND INTERFERENCE'S**

Sir:

Applicants hereby appeal, Pursuant to 37 C.F.R. 1.192(c), the Examiner's final rejection  
of Claims as set forth in the:

Five Advisory Actions dated February 25, 1999; and  
Final Office Action dated June 25, 1998

**REAL PARTY IN INTEREST**

The above-identified patent application has been assigned to the International  
Business Machines Corporation. The assignment has been recorded in the U.S. Patent  
and Trademark Office: Recordation date January 9, 1995; Reel/Frame 7331/0519.

## **RELATED APPEALS AND INTERFERENCES**

There are no related appeals and interferences.

Co-pending US application serial number 08/479,810 filed on June 7, 1995 is a division of the present application.

## **STATUS OF CLAIMS**

Claims 24-26, 86-90 and 96-177 are presently pending in the present application.

Claim 136 is allowed. Claims 24-26, 86-90, 96-135 and 137-177 have been finally rejected in the Office Action dated June 25, 1998 which provides the basis for this appeal.

The following table lists the independent claims and the claims which depend therefrom:

Set	Independent Claim	Dependent Claim
1	24	25, 26
2	86	87
3	88	90
4	96	97-102
5	103	104-108
6	109	
7	110	
8	111	
9	112	
10	113	
11	114	
12	115	
13	116	
14	117	
15	118	
16	119	
17	120	
18	121	
19	122	
20	123	
21	124	
22	125	
23	126	
24	127	
25	128	
26	129	164
27	130	165
28	131	166
29	132	167
30	133	168
31	134	169
32	135	170
33	136	171
34	137	172
35	138	173
36	139	174
37	140	175
38	141	176
39	142	177
40	143	144

## STATUS OF AMENDMENTS

On November 27, 1997, applicants submitted an amendment under 37 CFR 1.129(a) in response to the final rejection dated August 27, 1997. On May 14, 1997, applicants filed a supplementary response to the final rejection dated August 27, 1997. In response to these two submissions under 37 CFR 129(a), all pending claims except for claim 136 were finally rejected in the Final Action dated June 25, 1998. Applicants filed a notice of Appeal on December 28, 1998.

In the response to the Final Action dated June 25, 1998, applicants submitted the following Amendments after final rejection:

Amendments After Final Rejection:

November 25, 1998

December 10, 1998

December 11, 1998

December 14, 1998

December 15, 1998

December 15, 1998

December 15, 1998

December 18, 1998

December 22, 1998

December 27, 1998

In response the five Advisory Actions dated February 25, 1999 were received by Applicants. In response to these Advisory Actions three Amendments of the Final Rejection were submitted on June 14, 1999; June 15, 1999 and June 15, 1999. By telephone conversation the Examiner told applicants that these would be entered.

On June 24, 1999 Applicants resubmitted the amendment after final dated December 27, 1998 which the Examiner told the undersigned attorney was not received.

### **ISSUES**

1. Are claims 24-26, 86-90, 96-135 and 137-177 supported by the priority document?
2. Are claims 24-26, 86-90, 96-135 and 137-177 anticipated under 35 USC 102(a) by the Asahi Shinbum article?
3. Are the claims 24-26, 86-90, 96-135 and 137-177 obvious under 35 USC 103(a) in view of the Asahi Shinbum article?
4. Are claims 24-26, 86-90, 96-113, 129-131, 134, 135 and 139-142 not enabled under 35 USC 112, first paragraph.
5. Are claims 86-87, 96-108, 115, 118, 120, 122, 123, 124, 129-135 and 137-142 indefinite under 35 USC 112, second paragraph.

### **GROUPING OF THE CLAIMS**

Each claims is appealed individually.

## **SUMMARY OF THE INVENTION**

A method of flowing a superconducting electrical current in a transition metal oxide having a  $T_c$  greater than 26°K and maintaining the transition metal oxide at a temperature less than said  $T_c$ .

In a more particular aspect of the method of the present invention the transition metal is copper.

In another more particular aspect of the method of the present invention the transition metal oxide has a perovskite-like or a perovskite-type crystal structure which is a perovskite or near perovskite structure.

In another more particular aspect of the present invention the transition metal oxide has a layered-like or layered-type structure.

In another more particular aspect of the present invention, the composition includes a transition metal, a rare or rare earth like element, an alkaline earth element and oxygen.

## **ARGUMENT**

### **Priority**



The Examiner has acknowledged applicant's claim for priority under 35 USC §119 in the parent application, Serial No. 08/053,307 filed April 23, 1993. The certified copy has been filed in parent application, Serial No. 08/053,307, filed on April 23, 1993 as paper no. 28. (References to the priority document herein are to the corresponding European Patent Application 275 343 A1 published on July 27, 1988.)

Applicants respectfully disagree with the Examiner that support is not found in that certified copy for the invention as presently claimed.

In this regard the Examiner states:

Applicants' arguments filed April 11, 1996, January 3, 1996 and September 29, 1996, paper numbers 53, 50 and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996, paper numbers 49 and 52, have been fully considered but they are not deemed to be persuasive. The applicants quote some passages out of the priority document and argue that the present claims are fully based on that document. Nevertheless, that priority document is not deemed to provide basis for the limitations found in the present claims.

In this passage the Examiner states that "Applicants' arguments ... are not **deemed** to be persuasive" and "[n]evertheless, that priority document is not **deemed** to provide basis for the limitations found in the present claims." Webster's Ninth New Collegiate

Dictionary (Merriam-Webster Inc., Springfield, Mass. 1987) defines "deem" as a transitive verb meaning "to come to think or judge" and as an intransitive verb meaning "to have an opinion : believe." The examiner has used the intransitive form of the verb "deemed." The examiner has cited no statutory or case law authority which permits an examiner to object to a claim of priority based on the examiners "opinion" or "belief" that a priority document does not support applicant's claims. The Examiner must support a denial of a claim of priority based on what is actually stated in the priority document.

The examiner further states in support of the examiner's "opinion" or "belief" at page 3, paragraph 4.b;

- i. The recitation of a "composition including a transition metal, a rare earth or rare earth-like element, an alkaline earth element, and oxygen", as found in claim 86 (lines 2-4). The certified priority document may provide basis for the formula  $RE_2TM.O_4$  at p. 2, para. 4, but the claimed composition is deemed to be much broader than that formula.

Applicants respectfully disagree. In the priority document, for example in the abstract, RE is a rare earth element, TM is a transition metal and O is oxygen. The priority document further states at Col. 2, lines 22-25 "the lanthanum which belongs to the IIB group of elements is in part substituted by one member of the neighboring IIA group of elements...". Group IIA elements are the alkaline earth elements. The present specification teaches at page 11, lines 22-23, that RE stands for the rare earths (lanthanides) or rare earth-like elements. The "rare earth like element" act like a rare

earth element in the superconductive composition. Thus a rare earth-like element is an equivalent of rare earth element. Similar language appears in the present specification at page 12 lines 6--8, "the lanthanum which belongs to the IIB group of elements is in part substituted by one member of the neighboring IIA group of elements...". Therefore, the priority document teaches a "composition including a transition metal, a rare earth or rare earth-like element, and alkaline earth. Applicants note that in the passage quoted above, the Examiner incorrectly states that applicants claim a composition. This is not correct. Applicants claim a method of flowing a superconducting current in a transition metal oxide. In the last sentence of the passage quoted above the Examiner incorrectly states "the claimed composition is **deemed** to be much broader than [the] formula"  $RE_2TM.O_4$ ". The priority document is not limited to his formula. The composition taught by the priority document have variable amounts of oxygen, rare earth, rare earth-like and alkaline earth elements as is clearly shown in the abstract of the priority document.

The Examiner further states:

- ii. The limitation "non-stoichiometric amount of oxygen", as found in claim 6 and 86 (line 6). Basis may be seen for an oxygen deficit at p. 2, para. 4, but no such basis is seen for the more general limitation of "a nonstoichiometric amount of oxygen".

Applicants respectfully disagree. At Col. 3, lines 46-50 the priority document refers to applicants publication in Z. Phys. B - Condensed Matter 64 (1986) 189-193 which is

incorporated by reference in the present specification at page 6, lines 7-10. (This article is referred to here in as Applicants' article.) This article states at page 190, left col., lines 13-14 "[t]his system exhibits a number of oxygen-deficient phases with mixed-valent copper constituents." The priority document has various general formulas such as at Col. 3, lines 40, " $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$   $x < 1$  and  $y \geq 0$ ." The abstract has a more generic formula. A stoichiometric compound has a fixed amount of each element that make up the compound. Since, the amount of oxygen is variable, the formula has nonstoichiometric amounts of oxygen. Therefore, the priority document teaches nonstoichiometric amounts of oxygen.

In attachment A of this appeal, there are copies of pages 245 and 225 of Inorganic Chemistry by Moeler, John Wiley & Sons, Inc. 1952 and a copy of page 70 of Fundamentals of Chemistry, A Modern Introduction by Brescia et al., Academic Press, 1966. Attachment A provides an explanation of the terms stoichiometric and nonstoichiometric. The documents in Attachment A support applicants position that the priority document teaches nonstoichiometric amounts of oxygen.

The Examiner further states:

- iii. The limitation "a composition exhibiting a superconductive state" is found in present claim 88, (line 2). Wherein the certified priority document may provide basis for compositions of the formula  $\text{RE}_2\text{TM.O}_4$ , as

discussed above, but "transition metal oxide" and "superconductive state" are deemed to be much broader than the formula  $\text{RE}_2\text{TM.O}_4$ .

Applicants respectfully disagree. The field of the invention of the priority document is "a new class of superconductors in particular components ..." and the title is "New Superconductive Compounds ...". Applicants' article which is referred to in the priority document states at page 190, left Col., lines 14-16 from the bottom "X-ray powder diffractograms ... revealed three individual crystallographic phases." In the conclusion at page 192 the article states "[t]he system consists of three phases, one of them having a metallic perovskite-type layer-like structure. The characterization of the new, apparently superconducting, phase is in progress." Thus the priority document supports the limitation "a composition exhibiting a superconductive state". The general formula  $\text{RE}_{2-x}\text{AE}_x\text{TM.O}_{4-y}$   $x < 0.3$   $0.1 \leq y \leq 0.5$  and the more specific formula  $\text{RE}_2\text{TM.O}_4$  of the priority document is a composition; is a metal oxide; and is a transition metal oxide as recited in claims 24, 89 and 90. As noted above, the Examiner incorrectly implies that the priority document is limited to compounds having the formula  $\text{RE}_2\text{TM.O}_4$ .

The Examiner further states:

- iv. The limitation "a copper-oxide compound" is recited in claim 96 (line 6).
- 6). The certified priority document may provide basis for compositions of the formula  $\text{RE}_2\text{TM.O}_4$ , as discussed above, but "a copper-oxide compound" is not deemed to be equivalent to a composition of the

formula  $RE_2TM.O_4$ . Basis is not seen in the certified priority document for "a copper oxide compound" with the breadth of the present claims.

Initially the Examiner incorrectly implies claim 96 is directed to a copper oxide compound. Claim 96 is directed to a "copper oxide composition consisting essentially of a copper oxide compound having a layer-type perovskite-like structure." Applicants respectfully disagree. The priority document recites numerous copper oxide compositions. It is noted that the Abstract of the priority document refers to "[t]he superconductive compounds are oxides of the general formula  $RE_{2-x}AE_xTM.O_{4-y}$ , wherein RE is a rare earth, AE is a member of the group of alkaline earths or a combination of at least two members of that group, and TM is a transition metal, and wherein  $x < 0.3$  and  $0.1 \leq y \leq 0.5$ ." This formula permits no alkaline earth and a varying amount of alkaline earth, rare earths and a varying amount of oxygen. At column 3, lines 20 and 35, there is recited "the Ba-La-Cu-O system" and at line 41 " $La_{2-x}Ba_xCuO_{4-y}$   $x < 1$  and  $y \leq 0$  and at line 44 teaches  $La_{1-x}Va_xCuO_{3-y}$ . Thus the priority document provides support for a composition including a transition metal, a rare earth or rare earth-like elements, an alkaline earth element, an oxygen as found in applicants' claim, specifically claim 86. It is noted that at column 2, lines 13-19 the priority document states that "it is a characteristic of the present invention that in the compounds in question that the RE portion is partially substituted by one member of the alkaline earth group of metals, or by a combination of the members of this alkaline earth group and that the oxygen content is at a deficit." It is further noted that at column 2, lines 20-23 it states that "for example, one such compound that meets the

description given by this lanthanum copper oxide  $\text{La}_2\text{CuO}_4$  in which the lanthanum which belongs to the IIIB group of the elements is in part substituted by one member of the neighboring IIIA group of elements."

The priority document at column 3, line 6 recites Ti as a transition metal. It is noted that in claim 1 of the priority document, claim 1 recites the structure  $\text{RE}_{2-x}\text{AE}_x\text{TM.O}_{4-y}$  wherein TM is a transition metal. Claim 2 therein recites copper as the transition metal. Claim 3 therein recites nickel as the transition metal. Claim 8 therein recites chromium as the transition metal. Consequently, a broader class of transition metals other than copper is supported by the priority document.

It is clear from the quoted sections of the priority document that the priority document clearly supports a much broader composition than the Examiner is claiming that it does, and that the priority document, in fact, does support applicant's claims.

As noted above, the general formula of the priority document is much broader than the formula  $\text{RE}_2\text{TM.O}_4$  which the Examiner incorrectly states the priority document is limited to. The quantity of oxygen, the rare earth element and of an alkaline element is variable and the transition metal is not limited to copper. Consequently, the term "a copper-oxide compound" is adequately supported by the priority document.

The Examiner further states:

v. The limitation to the effect that "the copper oxide compound includes (including) at least one rare-earth or rare-earth-like element and at least one alkaline-earth element", as recited in claim 103 (lines 6 and 8). The certified priority document may provide basis for compositions of the formula  $RE_2TM.O_4$ , as discussed above, but basis is not seen for the more general limitation of "a copper-oxide compound" with a rare-earth (like) element and an alkaline earth element.

Applicants respectfully disagree. The second line of the abstract gives the general formula " $RE_{2-x}AE_xTM.O_{4-y}$   $x < 0.3$  and  $0.1 \leq y \leq 0.5$ ." In claim 1 of the priority document  $y \leq 0.5$ . Claim 2 recites RE is lanthanum and TM is a copper. Claim 3 recites RE is cerium and TM is nickel. Claim 4 recites RE is lanthanum and TM is nickel. Claim 8 recites RE is lanthanum and TM is chromium. Claim 9 recites RE is neodymium and TM is copper. Applicants' claim 103 recites "the copper-oxide compound including at least one rare-earth or rare-earth-like element and at least one alkaline-earth element". The priority document clearly supports this recitation. Applicants, as stated above, respectfully submit the Examiner is misrepresenting the priority document which refers throughout and, in particular, in the Abstract to "the general formula  $RE_{2-x}AE_xEM.O_{4-y}$  as stated above which includes a copper-oxide as stated above. The Examiner further states in the passage quoted above "but basis is not seen for the more general limitation of 'a copper-oxide compound' with a rare-earth (like) element and in alkaline earth element." It is noted that in the priority document, claim 2 refers to lanthanum as the rare earth; claim 3 refers to cerium as the rare earth; claim 5 refers to barium as a



partial substitute for the rare earth; claim 6 refers to calcium as a partial substitute for the rare earth; claim 7 refers to strontium as a partial substitute for the rare earth and claim 9 refers to neodymium as the rare earth. Clearly, the priority document uses barium, calcium and strontium. Consequently, the priority document supports the term rare earth-like since it includes elements (e.g. barium, calcium and strontium) other than those commonly referred to as the rare earth elements [which are elements 57-71] which satisfy the teaching of the priority document and of the present application. The Abstract of the priority document refers to "AE as a member of the alkaline earth or a combination of at least two members of that group". Consequently, the priority document clearly supports an alkaline earth element.

The Examiner further states:

vi. The limitation to the effect that "the copper-oxide compound includes at least one element (oxygen) in a nonstoichiometric atomic proportion", as found in claim 101 (lines 2 and 3), 102 (lines 2 and 3), 107 (lines 2 and 3), and 108 (lines 2 and 3). Basis may be seen for an oxygen deficit as discussed above, but no such basis is seen for the more general limitation of "a nonstoichiometric atomic proportion".

Applicants disagree for the same reasons given above for why the priority document supports "nonstoichiometric amount of oxygen".

The Examiner further states:

- vi. The limitation as to "the effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$ , as found in claim 103 (lines 13, 6 and 17). The critical temperature,  $T_c$ , is discussed throughout that certified priority document, but not  $T_{\rho=0}$ .

Applicants respectfully disagree.  $T_{\rho=0}$  is the temperature at which the bulk resistivity is about zero.  $T_c$  is the critical temperature or the temperature above which superconductivity does not exist. The priority document refers to applicants' article of which Figures 1,2 and 3 are the same figures as Figures 2, 3 and 4 of the present application. At page 22, lines 19-24, the present specification refers to Figure 4 of the specification stating "[i]ts resistivity decreases by at least three orders of magnitude, giving evidence for the bulk being superconducting below 13 K with an onset around 35 K, as shown in FIG. 4 on an expanded scale." When a superconductor is totally superconductive the resistivity,  $\rho$ , is zero. The temperature at which this occurs is  $T_{\rho=0}$ .

Applicants' article, (and thus the priority document), at page 191, right column, in referring to Fig. 1 thereof states "[u]pon cooling from room temperature, the latter exhibit a nearly linear metallic decrease of  $\rho(T)$ , then a logarithmic type of increase, before undergoing the transition to superconductivity." And in the sentence bridging pages 191-192 "[t]herefore, under the above premises, the peak in  $\rho(T)$  at 35 K, observed ... has to be identified as the start to superconductive cooperative

phenomena." And Applicants' article at page 192, left column, states "[u]pon cooling

below  $T_c$  ... the bulk resistivity gradually drops to zero by three orders of magnitude, for sample 2( Fig. 1)" From these statements in applicants article (which is referred to in the priority document) it is clear that the language objected to by the examiner is supported in the priority document.

In response to Applicants' arguments filed March 7, 1997 (#59) the Examiner states "they have been fully considered but not found to be persuasive".

The Examiner states:

i. The applicants quote portions out of the priority document and assert that those quoted sections "clearly (support) a much broader composition than the Examiner is claiming it does, and that the priority document, in fact, does support applicant's (sic) claim 86." The fact remains, nevertheless, that the priority document refers to the general formula  $RE_2TM.O_4$  in which the rare earth element (RE) may be partially substituted with a Group IIA metal. That disclosure in the priority document does not provide support for the broader limitations of the present claims, which do not limit the invention to that general formula.

As state above the Examiner incorrectly states that the priority document is limited to formula  $RE_2TM.O_4$ . This is clearly incorrect.

The Examiner further states:

ii. The applicants argue that the disclosure of varying amounts of oxygen in the priority document provides support for earlier priority for the term "non-stoichiometric amount of oxygen". Again, however, that disclosure in the priority document does not provide support for the broader limitations of the present claims, which do not limit the invention to those varying amounts.

It is not clear what the Examiner is trying to say in the last sentence of this quoted passage. The general formula in the Abstract of the priority document,  $RE_{2-x}AE_xTM.O_{4-y}$ , has the atomic amount of O varying from 0 to 4 independent of the atomic amount of RE, AE and TM. Thus the amount of O must have non-stoichiometric values. The Examiner's comments in the passage above are clearly in error.

The Examiner further states:

iii. The applicants urge that the disclosure in the priority document of the formula  $RE_2TM.O_4$  provides support for their limitations of "transition metal", "copper-oxide compounds", "rare earth or rare earth-like elements", and "alkaline earth element". Again, however, that disclosure in the priority document does not provide support for the broader

limitations of the present claims, which do not limit the invention to that formula.

The Examiner again incorrectly states that the priority document is limited to the formula  $\text{RE}_2\text{TM.O}_4$ . As stated above the examiner is clearly in error. The priority document supports a much broader formula than  $\text{RE}_2\text{TM.O}_4$ . As shown above, the priority document clearly supports applicants' claim limitations "transition metal", "copper-oxide compounds", "rare earth or rare earth-like elements" and "alkaline earth elements".

The Examiner further states:

iv. The applicants further "assume that the Examiner agrees with applicant's (sic) statements in their prior response in that the concept of the intercept temperature is well known in the prior art and can be included in claim 103." No basis is seen for that assumption. As noted in the previous Office Action and repeated above, the term " $T_{\rho=0}$ " is not found in the priority document. Well known or not, there is no basis for that term in the priority document.

For the reason given above the priority document clearly supports the term " $T_{\rho=0}$ ". Although this particular symbol is not used in the priority document, the priority document clearly shows that as temperature is decreased the resistivity of a

superconductor begins to drop in the value at the critical temperature  $T_c$  and goes to zero at another temperature, that is  $T_{\rho=0}$ . This symbol is just a short hand notation for that temperature. This property of superconducting materials is well known prior to applicants filing date, in fact that is what is meant by the term superconductor which is a material for which  $\rho=0$  for temperatures less than a certain temperature, i.e.,  $T_{\rho=0}$ . It is also well-known that: "[i]n the ideal case the resistance vanishes completely and discontinuously at a transition temperature.  $T_s$  ... Actually, the resistance temperature curve does fall more sharply the more specimen is like a single crystal ... [T]he drop always occurs in a measurable temperature range ..." (Theory of Superconductivity, M. von Laue, Academic Press, Inc., 1952) (See Appendix C of Applicants' response dated September 25, 1995). Moreover, the priority document at column 1, the first sentence of the Background of the Invention states "[s]uperconductivity is usually defined as the complete loss of electrical resistance of a material at a well defined temperature". That temperature is symbolically represented as  $T_{\rho=0}$ .

## CLAIM REJECTIONS - 35 USC § 102

Claims 24-26, 86-90, 96-135, and 137-177 have been rejected under 35 U.S.C. § 102(a) as being anticipated by Asahi Shinbum, International Satellite Edition (London), November 28, 1986 (hereinafter, "the Asahi Shinbum article").

The Examiner is stating that everything within applicants non-allowed claims is found in the Asahi Shinbum article. All of Applicants' non-allowed claims are dominant to (or generic to) the one allowed claim, claim 136. Thus by stating that all the non-allowed claims are anticipated, the Examiner is stating that the portion of each non-allowed claim which does not overlap the allowed claim is taught in the Asahi Shinbum article. This means that a person of skill in the art needs nothing more than what is taught in the Asahi Shinbum article to practice that part of each of Applicants' non-allowed claims which does not overlap Applicants' allowed claim.

The only parts of the Asahi Shinbum article which are relevant to applicants' claim are in the first paragraph:

A new ceramic with a very high  $T_c$  of 30K of the superconducting transition has been found. The possibility of high  $T_c$  - superconductivity has been reported by scientists in Switzerland this spring. The group of Prof. Shoji TANAKA, Dept. Appl. Phys. Faculty of Engineering at the University of Tokyo confirmed in November, that this is true.

in the second paragraph:

The ceramic newly discovered, is an oxide compound of La and Cu with Barium which has a structure of the so-called perovskite and shows metal-like properties. Prof. Tanaka's laboratory confirmed that this material shows diamagnetism (Meisner effect) which is the most important indication of the existence of superconductivity.

The Swiss scientist are the inventors of the present application. Thus this clearly refers to applicants work which was reported in Applicants article. These passages say that Prof. Tanaka confirmed applicants work. The newly discovered ceramic referred to in the article is the ceramic reported on in Applicants' article. The present applicant was filed less than one year after the publication of applicants' article. This article is a disclosure of Applicants' own invention and cannot be used as a reference against the present application.

Since the present application was filed within one year of Applicants' article, Applicants' article is not a reference as to them. Thus the only portion of the Asahi Shinbum article relevant to Applicants' claims is:

A new ceramic with a very high  $T_c$  of 30K of the superconducting transition ... is an oxide compound of La and Cu with Barium which has a structure of the so-called perovskite and shows metal-like properties.

Since the Asahi Shinbum article refers to " $T_c$  of 30K" and since each of Applicants claims recites  $T_c > 26$  °K, the Asahi Shinbum article alone cannot anticipate  $T_c > 26$  °K since to be an anticipation a reference must contain all the limitations of the claim it is said to anticipate. Also, the Asahi Shinbum article provides no teaching of how to made the "new ceramic". A reference which does not provide a method of making a composition cannot anticipate a claim to the composition and thus to a use of that new composition. Also, the Asahi Shinbum article has no specific embodiment of the new composition. Thus it cannot anticipate under 35 USC 102.



### **Applicants' Article Was in the US in Ready To File Form**

The issue involved here is straight forward. A third party reproduced and reported that fact in a written publication before of Applicants' filing date. The work of Applicants was reported in a written description published before the publication of the third party. Applicants filed the present application within one year of their publication, but after the third party publication. If Applicants did not file the present applicant within one year of the date of Applicants' article, Applicants' article would be a valid reference under 35 USC 102(a). But since Applicants filed the present application within 1 year of Applicants' article, it is not a reference under 35 USC 102(b).

35 USC 100 states the term "invention" means invention or discovery.

35 USC 102(a) states "[a] person shall be entitled to a patent unless ... the invention was known or used by others in this country, or patented or described in a printed publication in this or a foreign country, before the invention thereof by the applicants for patent."

Applicants invention or discovery was on or before April 17, 1986 which is the date Applicants submitted Applicants' article to Z.Phys.B. That article was published in September, 1986. Therefore, Applicants invented their invention prior to the date of the Asahi Shinbum article, November 28, 1986. Evidence submitted proving that applicants conception was in the United States at applicants direction prior to Nov. 28, 1986 is discussed below. In addition, the following evidence shows that Applicants' article was in this country in possession of IBM, the assignee, prior to the date of the Asahi Shinbum article. Attachment K of Applicants' response dated December 27, 1998, page 1, is a copy of the front cover of Zeitschrift Fur Physik B Condensed Matter Vol. 64 which contains Applicants' article ( pp 189-193) which is referred to and incorporated by reference at page 6, lines 6-10, of Applicant's specification. Applicants state at page 6 of the specification that Applicants' article is "[t]he basis or our invention". This page bears in the upper right the date stamp of the IBM Research

Library bearing the date of Sept. 18, 1986. Page 2 of Attachment K of Applicants' response dated December 27, 1998, is an enlarged view of the upper right corner showing the date stamp. Thus the assignee of the present invention, IBM, who was the employer of the inventors at the time of the conception of the invention, had in its possession in the United States, prior to the date of the Asahi Shinbum, a copy of the article which Applicants state forms the basis of their invention. Thus IBM had in its possession in the United States a written description of applicants' invention in "ready to patent form" ( as defined by the United States Supreme Court in Pfaff v. Wells 48 USPQ 2d 1641 decided November 10, 1998) prior to the date of the Asahi Shinbum article. The US Supreme Court held that "reduction to practice" is not needed to establish a date for invention. The court stated " [t]he statute's only specific reference to that term is found in §102(g), which sets fort the standard for resolving priority between two competing claimants to a patent." Since §102(g) is not applicable here, "diligence" and "reduction to practice" are not required. Applicants article in Zeitschrift Fur Physik "is proof that prior to [the date of the Asahi Shinbum article applicants have] prepared drawings or other descriptions of the invention that were sufficiently specific to enable a person skilled in the art to practice the invention." The Asahi Shinbum article sates that applicants' work was reproduced, by others, thus applicants article was sufficiently specific for a person of skill in the art to practice applicants' invention. Also, as stated in Applicants' response dated December 18, 1998, more than 5,200 articles refer to applicants article showing that applicants enabled the field of high T<sub>c</sub> superconductivity. Thus the Asahi Shinbum article is not a valid §102(a) reference against Applicants' claimed invention.

The Examiner states:

- ii. The applicants assert that the Asahi Shinbum article reports a third party's confirmation of their original discovery. That assertion appears to be correct, but the article still is deemed to be prior art under 35 USC 102(a).

(1) It should be noted again, however, that the applicants' discovery was not originally made in this country- and that they cannot show an earlier date than December 1986 for their invention in this country. The Asahi Shinbum article was published on November 28, 1986.

Applicants disagree with the Examiner. Applicants note that the Examiner acknowledges that the Asahi Shinbum article "confirms [Applicants'] original discovery." 35 USC 102(a) does not require applicants to show a date of invention in this country prior to the Asahi Shinbum article to avoid the Asahi Shinbum article being prior art. 35 USC 102(a) states "A person shall be entitled to a patent unless ... the invention was ... described in a printed publication in this or a foreign country, before the invention thereof by the application for patent." 35 USC 100 does not include reduction to practice in this country or conception in this country as part of the definition of invention. Only 35 USC 102(g) includes the language "reduction to practice" and "invention in this country". If Congress intended a reduction to practice to be necessary for a patent applicant to show that they invented their invention before the date of the printed publication, Congress would have included such language in the 35 USC 102(a). Also, if Congress intended that invention in this country was to be necessary for a patent applicant to show that they invented their invention before the date of the printed publication, Congress would have included such language in 35 USC 102(a).

In the final rejection the Examiner states:

- a. As discussed in paper no. 20 of the ancestral application, 07/053,307, it is not fully clear to what exact date applicants are entitled. Based on the record, nonetheless, that date would appear to be no later

than around December 13, 1986, the date samples were tested in the US to show superconductivity. See MPEP 715 et seq. The Asahi Shinbum article was published on November 28, 1986.

b. The reference confirms superconductivity in an oxide compound of La and Cu with Ba having a structure of the so-called perovskite structure. Although the reference fails to teach use of the testing of zero resistance for confirming superconductivity, it inherently must have been used because it is one of two methods used for testing for superconductivity (the other being diamagnetism). Accordingly, the burden of proof is upon the applicants to show that the instantly claimed subject matter is different from and unobvious over that taught by this reference."

In response to applicants' arguments filed April 11, 1996, January 3, 1996, and September 29, 1995, paper nos. 53, 50, and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996, paper nos. 49 and 52, the Examiner states they "are not **deemed** to be persuasive", that is it is the Examiner's **opinion** that they are not persuasive.

The Examiner cites *In re Brown*, 173 USPQ 685, 688; *In re Best*, 195 USPQ 430; and *In re Marosi*, 218 USPQ 289, 293 to support his rejection. These decisions are not directed to whether a reference is a valid §102(a) reference and are thus not relevant to this issue.

The Examiner is using Asahi Shinbum as a reference under 35 USC §102(a). Applicants disagree that this is proper since to do so does not permit applicants the one

year period provided under 35 USC §102(b) to file a US application after their own publication. The one year period permitted applicants to file the present application up to September 1987. The date of the Asahi Shinbum article November 28, 1986 is after the date of applicants' publication, but before the end of the one year.

Applicants believe that the Examiner has incorrectly applied 35 USC §102(a). The Court of Custom and Patent Appeal in *In re Katz* 215 USPQ 14, 17 states that:

It may not be readily apparent from the statutory language that a printed publication cannot stand as a reference under §102(a) unless it is describing the work of another. A literal reading might appear to make a prior patent or printed publication 'prior art' even though the disclosure is that of the applicant's own work. However, such an interpretation of this section of the statute would negate the one year period afforded under §102(b) during which an inventor is allowed to perfect, develop and apply for a patent on his invention and publish descriptions of it if he wishes.

Thus, one's own work is not prior art under §102(a) even though it has been disclosed to the public in a manner or form which otherwise would fall under §102(a). Disclosure to the public of one's own work constitutes a bar to the grant of a patent claiming the subject matter obvious therefrom only when the disclosure occurred more than one year prior to the date of the application, that is, when the disclosure creates a one-year time bar, frequently termed a "statutory bar," to the application under

§102(b). As stated by this court in *In re Facius*, 56 CCPA 1348, 1358, 408 F.2d 1396, 1406, 161 USPQ 294, 302 (1969), "But certainly **one's own invention, whatever the form of disclosure to the public, may not be prior art against oneself, absent a statutory bar.**" [Emphasis in original].

The Asahi Shinbum article states in the first paragraph, "The possibility of high T, superconductivity has been reported by scientists in Switzerland this spring". The "scientists in Switzerland" are the inventors of the present application. Applicants' invention was reported in Applicants' article which was submitted for publication in the Spring of 1986. The Asahi Shinbum article only reports the work of applicants and that it was reproduced by Prof. Tanaka. This article is a disclosure of applicants' "own invention" and cannot be used as a reference. Therefore, the Examiner is in error in rejecting Applicants claims 24-26, 86-90, 96-135 and 137-177 under 35 USC §102(a) as anticipated by Asahi Shinbum and under 35 USC §103 as obvious over Asahi Shinbum.

In regard to the two-year grace period under a prior statute corresponding to 35 USC §102(b) the U.S. Supreme Court in *Andrews v. Hovey*, 123 US 267 (1887) states that:

"The evident purpose of the section was to fix a period of limitation which should be certain, and require only a calculation of time, and should not depend upon the uncertain question of whether the Applicant had consented to or allowed the sale or use. Its object was to require the

inventor to see to it that he filed his application within two years from the completion of his invention, **so as to cut off all question of the defeat of his patent by a use or sale of it by others more than two years prior to his application**, and thus leave open only the question of priority of invention. The evident intention of congress was to take away the right which existed under the act of 1836 to obtain a patent after **an invention had** for a long period of time **been in public use, without the consent or allowance of the inventor**; it limited that period to two years, **whether the inventor had or had not consented to or allowed the public use.**"  
(Emphasis added)

From this quote from *Andrews v. Hovey*, it is evident that the use or sale by others prior to filing a patent application by the inventor does not cut off the inventor's right to obtain a patent so long as the inventor files the application within the statutory period which was 2 years at the time of the *Andrews v. Hovey* decision and is now 1 year under 35 USC 102(b). (Applicants note that the U.S. Supreme Court cited *Andrew Hovey* with approval in *Pfaff v. Wells*.) Thus Prof. Tanaka's reproducing of Applicants' results reported in Applicants' article and the reporting of this in *Asahi Shinbun* article does "not cut off [Applicants'] right to obtain a patent" since Applicants have filed the present application within one year of the date of publication of Applicants' article. Applicants note that the Supreme Court says that "the consent or allowance of the inventor" is not a factor in determining whether "a use" by another cuts off the one year period under §102(b).

The Patent Office Board of Appeals in *Ex parte Powell and Davies*, 37 USPQ 285 states in regard to the publication of applicant's foreign patent application before

the filing of a U.S. application on October 5, 1936 on an invention described in the foreign patent application that:

The Examiner has also rejected the claims on the printed specification of Applicants' own British application which appears from this record to have been published on August 27, 1936. We know of no authority for such a rejection. Neither section 3886 nor section 4887 R.S. warrants the rejection. Obviously, the publication could not have a date prior to Applicants' invention. **There is no statute that requires an Applicant to make his invention in this country.**

Therefore, Applicants of the present invention can rely on their publication in Zeitschrift for Physik as evidence of their invention. Applicants note that the Board states that the statute does not require Applicants to make the invention in this country to get the benefit of the one year period under 35 USC §102(b). Therefore, the date of Applicants' invention is as least as early as the date of Applicants' publication which is before the date of the Asahi Shinbum article.

The Patent Office Board of Appeals in Ex parte Powell and Davies, 37 USPQ 285, 286 further states:

The Commissioner indicates in Ex parte Grosselin that the Examiner should consider whether the German patent was derived from Applicant and was in effect nothing more than a printed publication of Grosselin's invention.

The Asahi Shinbum article states in the first paragraph:

A new ceramic with a very high  $T_c$  of 30K of the superconducting transition has been found. The possibility of high  $T_c$  - superconductivity has been reported by scientists in Switzerland this spring. The group of Prof. Shoji



TANAKA, Dept. Appl. Phys. Faculty of Engineering at the University of Tokyo confirmed in November, that this is true.

The "scientists in Switzerland" are the inventors of the above-identified application. The Asahi Shinbum article only reports the work of Applicants and that it was reproduced by Prof. Tanaka. This article is a disclosure of Applicants' "own invention" and clearly in the words of the Board in Ex parte Powell and Davies, "was derived from [Applicants] and [is] in effect nothing more than a printed publication of [Applicants'] own invention and cannot be used as a reference".

The Patent Office Board of Appeals in Ex parte Lemieux 148, 140 states that:

Finally, we believe that our holding is consistent with decisions in interference practice wherein, even though in the usual case a party may not establish a priority date of invention by reference to activity in a foreign country, yet in an originality case where a party is seeking to prove that the other party derived from him so that there is only a single original inventor, he may be permitted to prove derivation by reference to activity abroad. ... By analogy, in the present case appellant has demonstrated that he is the single original inventor, there being no adverse party.

Following this decision it is clear from the Asahi Shinbum article that Applicants are the "single original inventor" and that the Asahi Shinbum article is "derived" from Applicants and that Professor Tanaka's work reported in the Asahi Shinbum article is "derived" from Applicants.

In In re Mathews 161 USPQ 276 (CCPA 1969) a patent to Dewey was cited under 35 USC 102(e) against the application of Mathews. The Dewey patent disclosed but did

not claim the invention claimed in the Mathews application. The claimed invention in the Mathews application was a circuit which Dewey disclosed to comply with 35 USC 112 requirements. Mathews submitted Dewey's affidavit under 37 CFR 132 which stated that Mathews disclosed to Dewey the circuit which Dewey described but did not claim. The CCPA held that Dewey was not a reference under 35 USC 102(e) against Mathews application stating 162 USPQ 276, 278:

It necessarily follows that Dewey may not be relied upon to defeat Mathews' application since Dewey's disclosure, *in view of the facts established in the record*, is not inconsistent with the novelty of Mathews' claimed invention, That is, *on the record here*, Dewey derived his knowledge from Mathews who is "the original, first, and sole inventor."

Following *In re Mathews*, it is necessary follows that the Asahi Shinbum article cannot be relied upon under 35 USC 102(a) to defect the present application since the Asahi Shinbum article states that Prof. Tanaka derived his knowledge from applicants who are the original, first, and sole inventors.

*In re Mathews* is directed to a reference under 35 USC 102(e) and not under §102(a). But this does not matter since under §102(e) an issued patent (which corresponds to a printed publication under §102(a)) is a reference as of the filing date (which corresponds to the publication date of a printed publication under §102(a)) and not the publication date (the issue date) of the §102(e) cited patent. Also, if the patent

cited as a §102(e) reference had issued prior to the filing date of the applicant in In re Mathews, it would have been a §102(a) reference. Thus the rationale of In re Mathews should apply to a reference cited under §102(a). The Asahi Shinbun article states that Prof. Tanaka derived his knowledge from Applicants' article and that Prof. Tanaka reproduced Applicants' work reported in Applicants' article and thus Applicants are the original, first and sole inventor.

In response to applicants' comments on the cited decisions, the Examiner states, "The applicants cite four decisions which do not directly apply to the present facts."

Applicants disagree.

In regards to In re Katz the Examiner states:

(a) The In re Katz decision held that an applicant may overcome an article as 35 USC 102(a) prior art by showing that the applicant was a co-author and that the other co-authors were under the direction and control of the applicant. Here, however, the applicants were neither co-authors in the Asahi Shinbun article nor did they exercise direction and control over the work reported in that article.

Applicants disagree. The Examiner does not cite the text of In re Katz to support this interpretation of In re Katz. In fact, In re Katz does not support the Examiner's position. In In re Katz an article co-authored by the patent applicant was cited against

the applicants' patent application under 35 USC 102(a). The application was filed less than one year after the article. In determining whether the article was prior art under 35 USC 102(a), the CCPA states "[i]t may not be readily apparent from the statutory language that a printed publication can not stand as a reference under §102(a) unless it is describing the work of another." 215 USPQ 14, 17. The inventor submitted a declaration stating that he was the sole inventor of the subject matter described in the article and that the other authors were students working under his direction. The CCPA concluded that "The applicant's declaration is sufficient in this case to overcome the rejection" under 35 USC 102(a). 215 USPQ 14, 18. There is no evidence of record that the Asahi Shinbum article describes any invention other than those of Applicants. In this regard the CCPA further states:

As an initial matter, we hold that authorship of an article by itself does not raise a presumption of inventorship with respect to the subject matter disclosed in the article. Thus, co-authors may not be presumed to be coinventors merely from the fact of co-authorship. On the other hand, when the PTO is aware of a printed publication, which describes the subject matter of the claimed invention and is published before an application is filed (the only date of invention on which it must act in the absence of other proof), the article may or may not raise a substantial question whether the applicant is the inventor. **For example, if the author (whether he is the applicant or not) specifically states that he is describing the work of the applicant, no question at all is raised.** The content and nature of the printed publication, as well as the circumstances surrounding its publication, not merely its authorship, must be considered. (Emphasis added).

It is clear from this passage that where the authors of an article are not the inventors of an invention described therein, the article is not necessarily a 102(a) reference. The above passage states "if the author (whether he is the applicant or not) specifically states that he is describing the work of applicants, no question at all is raised", that the article is not a reference under § 102(a). The Asahi Shinbum article clearly states that Prof. Tanaka reproduced applicants work reported in Applicants' article. There can be no question that the Asahi Shinbum article is not a reference under § 102(a). Moreover, "the content and nature" of the Asahi Shinbum article "as well as the circumstances surrounding the publication" clearly show that it is describing Prof. Tanaka's reproduction of Applicants' work. A published article is an invitation to all readers to reproduce and verify the work reported. Thus the Asahi Shinbum article describes no invention other than that of Applicants.

In regards to *Andrews v. Hovey* the Examiner states:

(b) The *Andrews v. Hovey* decision involved a grace period which is now codified in 35 USC 102(b). The present case involves a printed publication as prior art under 35 USC 102(a).

The Examiner's comments miss the point of *Andrews v. Hovey*. As stated above, this case clearly says that "the use" by others prior to filing of the patent application by the inventors (which would be a §102(a) reference) does not cut off the right of the inventors to obtain a patent on the application filed within the statutory period under

§102(b) from the inventors own printed publication. The Asahi Shinbum article describes "the use" of Applicants' invention by Prof. Tanaka. If such a use in the United States would not be prior art under §102(a), it is not possible for a printed publication describing such a use in a foreign country to be prior art under §102(a).

In regard to Ex parte Powell and Davies:

(c) The Ex parte Powell and Davies" decision held that an applicant's own foreign patent which issued within the grace period cannot be used against him or her.

The Examiner's comments miss the point of Ex parte Powell and Davies which explicitly states that "[t]here is no statute that requires an Applicant to make his invention in this country". Applicants initially made there invention in Zurich, before the date of the Asahi Shinbum article. Their results were published prior to the Asahi Shinbum article in Applicants' article which was in possession of the assignee of the present invention in the US prior to the date of the Asahi Shinbum article. Also, in Ex parte Powel and Davies the Applicant's British application was published before their application was filed in the United States and it was still not a valid §102(a) reference.

In regard to Ex parte Lemieux, the Examiner states

The Ex parte Lemieux" decision applied that reasoning to an applicant's own article published in another country. Again, the present applicants had no part in the writing of the Asahi Shinbum article.

Again the Examiner's comments miss the point of Ex parte Lemieux which states "in an originality case where a party is seeking to prove that the other party derived from him so that there is only a single original inventor, he may be permitted to prove derivation by reference to activity abroad". Here the Asahi Shinbum article says that Prof. Tanaka derived his work from the work of Applicants and thus the Asahi Shinbum article is not a reference against the present application.

In regard to In re Mathews the Examiner states:

"In re Mathews, 161 USPQ 276, 277-279 (CCPA 1969), held that an applicant may overcome a patent as prior art under 35 USC 102(e) with evidence that the applicant provided the knowledge for the disclosure in that patent. By contrast, the present facts involve prior art under 35 USC 102(a) with a publication date before the invention was in this country."

In the present Application the Asahi Shinbum article acknowledges that Applicants provided the knowledge to Prof. Tanaka to reproduce Applicants work which is described in Applicants' article. And since the Asahi Shinbum article refers to Applicants' discovery, as stated above, for this purpose a §102(a) reference is equivalent to a 102(e) reference.

The Examiner further states:

(3) The present facts may raise a novel issue of law." The applicants were the first to develop the presently claimed invention, but the earliest

date they can show that invention in this country is December of 1986." The Asahi Shinbum article was published in November of 1986 and describes the development of superconductivity with an oxide of La, Ba, and Cu having a perovskite structure by a third party, but that article apparently indicates that the third party was confirming the discovery of the present applicants. Notwithstanding the possible uniqueness of the present facts, however, the Asahi Shinbum article still is deemed to be prior art under 35 USC 102(a), which the applicants have not been able to overcome with a showing of an earlier date in this country or a showing of their direction and control over the work done by that third party.

35 USC §102(a) and the cited case do not require work at an earlier date in this country to overcome reference cited under §102(a). Also, §102(a) and the cited case law do not require a showing that the Applicants exercised direction and control over Prof. Tanaka or the author of the Asahi Shinbum article. In fact, 35 USC §102 and the cited cases require a contrary result as Applicants have shown above. Notwithstanding, Applicants have shown that their conception was in this country in ready to file form, in the possession of the assignee of the present invention, prior to the date of the Asahi Shinbum article.

Applicants have argued that if one would follow the rationale of the Examiner, that is, if an applicant publishes an article and some other third party reports that same result prior to applicant's filing of a patent application which is subsequently filed within one year of applicant's own publication, the reporting of applicant's work by the third party would be prior art against applicant's application. Such a result would



deny (the applicant) the one year grace period provided under 35 USC 102(b). The Examiner dismisses this argument saying

“applicants” argument is duly noted, but again, it is further noted that the reference is prior art under 35 USC 102(a). The reference is not just a republication of the applicants' article. Instead, the reference is the reporting of someone else's work which confirms the applicants' work. The applicants also are not able to show a priority date which pre-dates the publication of that reference”.

The Examiner is ignoring the fact that the Asahi Shinbum article and the work of Prof. Tanaka reported on therein was derived from Applicants. The cases cited above clearly state that when a third party derives their knowledge from an applicant, the third party's knowledge, for use or for publication of the information is not prior art against such an applicants' patent application.

### **Applicants Have Proven They Can Swear Behind the Reference**

Even though, as stated by the U.S. Supreme Court in Pfaff v. Wells, it is not necessary to show anything more than a conception to establish a date of invention under all sections of 35 USC 102 other than §102(g). Applicants have proven by facts that the conception of their invention was in the United States at their direction prior to the date of the Asahi Shinbum article, November 28, 1986, and applicants have proven that they were diligent from prior to the date of the Asahi Shinbum article by instructing coworkers in the United States until December 3, 1986 which is the date the Examiner

believes is the earliest date of Applicants reduction to practice in the United States. (For the reasons of record applicants believe that they have shown that their invention was reduced to practice in the United States prior to the date of the Asahi Shinbum article). The examiner has not rebutted applicants proof that applicants conception was in the United States at their direction prior to the date of the Asahi Shinbum article and the Examiner has not denied that applicants have proven that they were diligent by instructing coworkers in the United States from a time prior to the date of the Asahi Shinbum article until the date the Examiner believes is the date of Applicants' date of reduction to practice in the United States. The details of Applicants' proof are discussed at pages 22, line 8 to page 24, last line, of applicants' Substitute Amendment dated March 6, 1997. That argument is reproduced in detail below.

The Examiner's response to Applicants' proof is at page 19, paragraph d. ii of the final rejection "[t]he applicants further urge that they have shown clear diligence from before November 28, 1996 until actual reduction to practice at or around December 3, 1986. Nevertheless, the actual reduction in this country is deemed to have occurred on December 3, 1986, which is after the publication date for the reference." (As stated above the Examiner is in error that Applicants have to prove reduction to practice in this country before the date of the Asahi Shinbum article to avoid it as a §102(a) reference.)

Willson v. Sherts 81 F 2d 775, 28 USPO 379 (CCPA 1936) held (in an interference) that an inventor who conceives an invention outside of the United States

gets the benefit of the date that a third party, to whom the invention is disclosed, brings the conception into the United States (28 USPQ 379, 381) and that acts in this country done on behalf of the inventors can be used to show diligence to reduction to practice in the United States (28 USPQ 379, 383). Thus, the rejections of Applicants' claims under 35 USC 102 and 103 over the Asahi Shinbum article should be withdrawn.

It is noted that in the declaration of co-inventors J. G. Bednorz and K. A. Mueller dated March 21, 1988, mailed into the patent office on June 22, 1988 at paragraph 3, states "On approximately October 16, 1986, we gave Praveen Chaudhari ... six samples of the high temperature superconductive ceramic oxide materials that we had described in our aforementioned Z Physik B. publication. Praveen Chaudhari brought these samples back to the U.S. when he returned after visiting with us on or about October 16, 1986." This is evidence that these samples are brought into the United States on or about October 16, 1986. When these samples came into the United States, since they were inherently superconductive as claimed, the invention was essentially reduced to practice in the United States on that date. It is further noted that the Declaration of Alexis P. Malozenoff signed March 30, 1988 states at paragraph 3, "On or about November 15, 1986, Richard Greene and I traveled to Baltimore for a magnetics conference. During our travel to Baltimore, we discussed Greene's ongoing experiments in high  $T_c$  superconducting samples which he said had been received from Bednorz and Mueller." This is clear evidence that by November 15, 1986, superconducting samples fabricated by applicant's were being measured in the United States. These samples were inherently superconducting and, consequently,

established the reduction to practice in the United States as of that date. The Declaration of Cheng-Chung John Chi dated March 29, 1988 states at paragraph 2, "At a time prior to approximately the middle of November, 1986, Chang C. Tsuei told me a measurement he made on  $T_c$  superconducting material which he said were received from Georg Bednorz and K. A. Mueller, two physicists working for IBM Corporation in Zurich, Switzerland ... Chang Tsuei said that he had measured resistivity versus temperature of these samples." This is again further evidence that the Mueller Bednorz superconducting samples were in the United States prior to the middle of November 1986."

In the Affidavit of Sung Il Park, dated March 30, 1988, at paragraph 4, it is stated "the preparation in measurement of the aforementioned superconducting samples occurred at a date prior to November 15, 1986, and to the best of my recollection, occurred on or about November 9, 1986, the date when a Helium dower was pumped down preparatory to taking the actual measurement." Therefore, since measurements were taken prior to the date of publication of the Asahi Shinbum article, which was November 28, 1986 the invention was reduced to practice in the US prior to the publication date of the Asahi Shinbum article.

At page 11 of the Examiner's Action dated April 19, 1996, in the paragraph labeled i, the Examiner states "the applicants argue that Sung Il Park affidavit of March 30, 1988 states at para. 4 that measurements were taken of a superconductive sample on or before November 9, 1986, to the best of affiants recollection, or no later than

November 15, 1986. The document evidence is not deemed to support that argument, however." In the paragraph marked (1) on page 11 of PA, the Examiner states "plots of those measurements are missing. See the Cheng C. Tseui affidavit of March 30, 1998, para. 6." This statement comes directly out of Cheng Tseui's Declaration. Notwithstanding, Cheng Tseui's Declaration says the measurements were made, that the plots that were taken were missing. The last sentence of this paragraph states "I believe that they may have been inadvertently thrown away when the laboratory was subsequently extensively cleaned." The Examiner further states "a hand-drawn diagram with the indication of a vacuum pumped down on November 8, 1988 also is not deemed to show that the measurements were taken." The Examiner is referring to paragraph 5 of the Cheng Tseui Declaration and Exhibit C which contains the hand-drawn figure.

At paragraph (2) of page 11 of the Examiner's Action dated April 19, 1996, the Examiner points to cablegrams sent by Dr. Greene to applicants in Zurich which are attached as Exhibit B to his Declaration. The Examiner states "Dr. Greene reports that no indication of superconductivity has been seen in his specific heat measurements for temperature 4-35°K." The Examiner fails to note that in the same cablegram dated November 11, 1986, Dr. Greene states "this is not really too surprising given the very broad transition to have found in resistivity and susceptibility." The Examiner acknowledges that "Exhibit C has pages dated December 1, 1986 on in Exhibit D, which actually has plots and resistance versus temperature dated as early as December 3, 1986." The Examiner is conceding that high  $T_c$  superconductivity was

measured on the samples which the very same set of cablegrams and affidavit say were in the United States in the middle of November 1986. Consequently, by Examiner's own admission, samples which were in the United States were clearly shown to be superconducting as of December 3, 1986. Consequently, the samples that were in the United States as of November 9 were inherently superconducting. It is clear from the same declarations that Applicants' were communicating with Dr. Greene. It is noted that Dr. Greene's cablegram dated November 25, 1986 to applicants states he will resume work on the new superconductor and that not much will happen because of the Thanksgiving Holiday until the following week. There are cablegrams dated November 26, December 1, December 2, 1986 related to high  $T_c$  superconductivity. Dr. Greene's Exhibit C has notebook pages dated December 1, 1986 to December 5, 1986. The December 5, 1986 shows  $T_c$  of 26°K and 30°K. Exhibit D show a plot of R vs. T dated December 8, 1986. Clear reduction to practice is shown and clear diligence is shown from prior to the date of the Asahi Shinbum article. This was clearly done in close correspondence with the applicants. Thus, the facts clearly shown applicant's can swear behind the Asahi Shinbum reference.

The Examiner repeats the same arguments in the final rejection without rebutting Applicants' arguments and proof that their conception was in this country at their direction and that their co-inventors in this country under their direction diligently pursued a reduction to practice in this country the earliest date of which according to the Examiner is December 3, 1986.

## **Applicants Invention Was Reduced To Practice In the US Before**

### **The Asahi Shinbum Article**

Attachment C of this Brief is a copy of a letter from C. W. Chu to Applicants dated December 3, 1986. This letter states:

This is just to inform you that my group at the U. of Huston has reproduced your results (Z. Phys. B 64, 189 (86)) three weeks ago. ... I believe it is superconductivity.

A journal article is an invitation to any one to reproduce the work reported therein . Thus a reader of the article is for that purpose under the diredtion and control of the author. Thus Applicants invention was reduced to practice in this country prior to the date of the Asahi Shinbum article at the direction and control of Applicants.

The Examiner in the final rejection repeats the earlier rejection stating:

i. The applicants argue that the Sung 11 Park Affidavit of March 30, 1988 states at para. 4 that measurements were taken of a superconductive sample on or before November 9, 1986, to the best of the affiant's recollection, or no later than November 15, 1986. The documentary evidence is not deemed to support that argument, however. See MPEP 715.07.

(1) Plots of those measurements are missing. See the Chang C. Tsuei Affidavit of March 30, 1988, para. 6. A hand-drawn diagram with the

indication of vacuum pumping on November 9, 1988 also is not deemed to show that the measurements were taken.

(2) Moreover, the other evidence in the record appears to show that high temperature superconductivity was not attained in this country as of November 9 or 15, 1986. The March 30, 1986 Declaration of Richard L. Greene includes a series of cablegrams sent by Dr. Greene to the applicants in Zurich, Switzerland as Exhibit B. On both November 11, 1986 and November 14, 1986, Dr. Greene reports that no indication of superconductivity has been seen in his specific heat measurements for temperatures of 4-35°K. Exhibit C has pages dated December 1, 1986 on, and Exhibit D, which actually has plots of resistance vs. temperature, has an earliest date of December 3, 1986.

i. The applicants argue that "Praveen Chaudhari brought these samples back to the U.S. when he returned after visiting (the inventors) on or about October 16, 1986. When these samples came into the United States since they were inherently superconductive as claimed, the invention was essentially reduced to practice in the United States on that date." As stated before repeated above, however, the applicants were unable to show the attainment of superconductivity any earlier than December 3, 1986 in this country. Again, the present invention is directed to the method of superconducting electricity. That method apparently was not reduced to practice before December 3, 1986.

ii. The applicants further urge that they have shown clear diligence from before November 28, 1986 until actual reduction at or around December 3, 1986. Nevertheless, the actual reduction in this country is deemed to have occurred on December 3, 1986, which is after the publication date for the reference.



iii. The applicants assert that they should be entitled to a one-year grace period for their own published invention, but this prior art rejection is based on 35 USC 102(a) because the author of that reference is a different inventive entity.

19 The applicants' proposed priority date for the EPO application is January 23, 1987, which is after the December 1986 dates show by the Richard L. Greene Affidavit.

In these repeated rejections the Examiner has not responded to Applicants' arguments and thus has not rebutted any of them. Therefore, the Examiner concedes that Applicants' conception was in this country at their direction prior to the date of the Asahi Shinbum article and that coworkers in this country at Applicants' direction diligently reduced their invention to practice in the United States. Applicants petitioned for withdrawal of the final rejection requesting the reasons for why the 1.132 affidavits submitted did not effectively swear behind the Asahi Shinbum article. The petition was denied by the Director of Group 1700 without rebutting applicants proof of conception and diligence. Therefore, the Director of Group 1700 concedes that Applicants' conception was in this country at their direction prior to the date of the Asahi Shinbum article and that coworkers in this country at Applicants' direction diligently reduced their invention to practice in the United States. This necessarily requires a finding that the Asahi Shinbum article is not a valid §102 reference.

Therefore, the Board is respectfully requested to reverse the rejection of claims 24-26, 86-90, 96-135 and 137-177 under 35 USC § 102(a) as anticipated by Asahi Shinbum article.

## CLAIM REJECTIONS - 35 USC § 103

Claims 24-26, 86-90, 96-135 and 137-177 have been rejected under 35 U.S.C. § 103(a) as being unpatentable over Asahi Shinbum article.

Claim 136 has been allowed over the Asahi Shinbum article since according to the Examiner the examples in the present specification are deemed to show criticality for the formula of claim 136.

Since the present application was filed within one year of Applicants' article, Applicants' article is not a reference as to them (even though it would be a reference as to a third party). Thus the only portion of the Asahi Shinbum article relevant to Applicants' claims is:

A new ceramic with a very high  $T_c$  of 30K of the superconducting transition ... is an oxide compound of La and Cu with Barium which has a structure of the so-called perovskite and shows metal-like properties.

Since the Asahi Shinbum article refers to " $T_c$  of 30K" and since each of Applicants claims recites  $T_c > 26$  °K, the Asahi Shinbum article alone cannot anticipate  $T_c > 26$  °K since to be an anticipation a reference must contain all the limitations of the claim it is said to anticipate. Also, the Asahi Shinbum article provides no teaching of how to make the "new ceramic". A reference which does not provide a method of making a composition cannot anticipate a claim to the composition and thus to a use of that new composition. Also, the Asahi Shinbum article has no specific embodiment of the new composition. Thus it cannot anticipate under 35 USC 102. If as to Applicants the Asahi Shinbum article is not a valid §102 reference, the Asahi Shinbum article cannot render Applicants' claims obvious since to do so would render the Asahi Shinbum article a valid §102 against Applicants.

As state above the examiner's characterization of the Asahi Shinbum article does not accurately represent the teaching of this article.

Applicants' article which is incorporated in applicants' specification and priority document is directed to a Ba-La-Cu-O system. Applicants' article was submitted for publication on April 17, 1986 to Z. Phys. B from the IBM Zurich Research Laboratory in Switzerland. Thus the only teaching in the Asahi Shinbum article relevant to Applicants' claimed invention is the teaching in Applicants' article which is incorporated by reference in the present application and referred to in the priority document. The Asahi Shinbum article provides no teaching relevant to applicants' claimed invention other than the teaching in Applicants' article on how to make the ceramic "newly discovered" by applicants. The Asahi Shinbum article states the Applicants' "newly discovered" ceramic "is an oxide compound of La and Cu with Barium which has a structure of the so-called perovskite and shows metal-like properties". This is described in detail in Applicant's article. Thus the examiner is stating that it is obvious to a person of skill in the art to practice the invention of all of applicants non-allowed claims from the teaching of the Asahi Shinbum article which is the teaching of Applicants' specification which incorporates applicants' article by reference. Applicants note that they received the Nobel Prize in Physics in 1987 for their discovery reported in applicants article. Since Prof. Tanaka apparently only reproduced applicants work based on applicants' article, he did not share in the Nobel prize. Therefore, the examiner is stating that all of applicants non-allowed claims are obvious in view of applicants' teaching.

Alternatively, the examiner is stating that all of applicant's non-allowed claims are obvious in view of the Asahi Shinbum article's statement that "[a] new ceramic with a very high  $T_c$  of 30 K of the super conductive transition has been found. ... The ceramic newly discovered, is an oxide compound of La and Cu with Barium which has a structure of the so-called perovskite and shows metal-like properties. " Thus the examiner is stating that once a person of ordinary skill in the art knows that "an oxide compound of La and Cu with Barium which has a structure of the so-called perovskite and shows metal-like properties " has a "a very high  $T_c$  of 30 K" the inventions of all of applicants non-allowed claims can be made and used by such a person of ordinary skill in the art without any additional teaching other than what is known by a person of ordinary skill.

Applicants acknowledge that if a material is known to be a superconductor, a person of skill in the art would know to cool the material to below the  $T_c$  and to flow a superconducting current therein at that temperature. Prior to the date of Applicants' invention, which is at least as early as the date on which Applicants' article was published by Z. Phys. B no one knew that transition metal oxides had a  $T_c > 26$  K except for Applicants. As stated above the Asahi Shinbum article describes no invention other than that of Applicants and is thus not a valid reference.

Therefore, the Board is respectfully requested to reverse the rejection of claims 24-26, 86-90, 96-135 and 137-177 under 35 USC §103 as obvious over the Asahi Shinbum article.



## OBJECTION TO THE SPECIFICATION UNDER 35 USC 112

The examiner states:

5. The specification is objected to under 35 U.S.C. § 112, first paragraph, as failing to provide an enabling disclosure commensurate with the scope of the claims.

Applicants disagree. The specification incorporates by reference Applicants' article. In the rejection under 35 USC 102 and 103 over the Asahi Shinbum article, the examiner has stated that a person of skill in the art is enabled to practice the inventions of applicants' non-allowed claims by the mere statement that a Ba-La-Cu-O compound has been confirmed to be superconductive as described by Applicants in their article. The examiner's objection to the specification is inconsistent with the examiner's rejection under 35 USC 102(a) and 103(a).

The text of the Asahi Shinbum article merely states that Prof. Tanaka reproduced Applicants' work. Thus, the Examiner has stated that all of the inventions of applicants' non-allowed claims are contained within the Asahi Shinbum article and thus are fully enable by Applicants' article. The Examiner has also rejected all of applicants' non-allowed claims under 35 USC §103(a) in view of the Asahi Shinbum article. This means that nothing more is needed than what is described in Applicants' article and ordinary skill to practice all of Applicants non-allowed claims.

The examiner further states:

- a. The present specification is deemed to be enabled only for compositions comprising  $\text{Ba}_x\text{La}_{5-x}\text{CuO}_y$ .

The examiner again used the terminology “deemed” which means that it is the examiner’s “opinion”. The examiner has introduced no factual evidence to support the examiner’s “opinion” that “[t]he present specification is deemed to be enabled only for compositions comprising  $\text{Ba}_x\text{La}_{5-x}\text{CuO}_y$ .” As shown below, the specification cites a substantially large number of specific compositions, and provides sufficient teaching to enable a person of skill in the art to practice Applicants’ invention.

The examiner further states:

The art of high temperature (above 30 K) superconductors is an extremely unpredictable one. Small changes in composition can result in dramatic changes in or loss of superconducting properties. The amount and type of examples necessary to support broad claims increases as the predictability of the art decreases. Claims broad enough to cover a large number of compositions that do not exhibit the desired properties fail to satisfy the requirements of 35 USC 112. Merely reciting a desired result does not overcome this failure. In particular, the question arises: Will any layered perovskite material containing copper exhibit superconductivity? Also, does any stoichiometric combination of rare earth, an alkaline earth, and copper elements result in an oxide superconductor?

The examiner provides no factual evidence to support the statement “[t]he art of high temperature (above 30 K) superconductors is an extremely unpredictable one.” This is an opinion of the examiner. The examiner should withdraw the rejection, provide



factual evidence to support the opinion or submit an examiner's affidavit under MPEP 706.02(a) qualifying himself as an expert in the art of high T<sub>c</sub> superconductors to offer such a conclusory opinion. Applicants requested such an Examiner's affidavit. Since the Examiner has not provided such an affidavit, the Examiner's opinions should be disregarded. It is Applicants' teaching that controlling the amount of the constituents of the composition, such as oxygen content, effect the superconductive properties of the composition. It is a matter of routine experimentation to find the optimum constituents, such as oxygen content, for a particular high T<sub>c</sub> superconducting composition. Applicants do not have to provide experimental results for every composition that fall within the scope of their claims when a person of skill in the art exercising routine experimentation has a reasonable expectation of success following applicants teaching to achieve a composition through which can be flowed a superconducting current according to the teaching of Applicants' specification.

According to *In re Angstadt* 190 USPQ 214, 218 in an unpredictable art, §112 does not require disclosure of a test with every species covered by a claim. The CCPA states:

To require such a complete disclosure would apparently necessitate a patent application or applications with "thousands" of examples or the disclosure of "thousands" of catalysts along with information as to whether each exhibits catalytic behavior resulting in the production of hydroperoxides. More importantly, such a requirement would force an inventor seeking adequate patent protection to carry out a prohibitive number of actual experiments. This would tend to discourage inventors

from filing patent applications in an unpredictable area since the patent claims would have to be limited to those embodiments which are expressly disclosed. A potential infringer could readily avoid "literal" infringement of such claims by merely finding another analogous catalyst complex which could be used in "forming hydroperoxides."

The Examiner provides no evidence to support the examiner's statement that "[t]he amount and type of examples necessary to support broad claims increases as the predictability of the art decreases." The examiner has provided no evidence that the predictability of art of high  $T_c$  superconductivity is low. The Examiner's statement that "[c]laims broad enough to cover a large number of compositions that do not exhibit the desired properties fail to satisfy the requirements of 35 USC 112." implies that applicants' claims "cover a large number of compositions that do not exhibit the desired properties" of high  $T_c$  superconductors. The Examiner has provided no evidence to support the examiner's implication. In fact, the claims do not cover any compositions that do not exhibit the desired properties of high  $T_c$  superconductors. Applicants' claims only cover superconductors having  $T_c > 26^\circ\text{K}$  which carry a superconductive current. Applicants' claims are not composition of matter claims.

The Board's attention is directed to the following comments from the specification.

The specification states at page 1, lines 5-10, that "This invention relates to ... superconducting compositions including copper and/or transition metals."

The specification further states at page 5, lines 2-9 that:

"It is another object of the present invention to provide novel superconductive materials that are multi-valent oxides including transition metals, the compositions having a perovskite-like structure."

It is a further object of the present invention to provide novel superconductive compositions that are oxides including rare earth and/or rare earth-like atoms, together with copper or other transition metals that can exhibit mixed valent behavior."

The specification further states at page 8, lines 1-11, that "[A]n example of a superconductive composition having high  $T_c$  is the composition represented by the formula RE-TM-O, where RE is a rare earth or rare earth-like element, TM is a nonmagnetic transition metal, and O is oxygen. Examples of transition metal elements include Cu, Ni, Cr etc. In particular, transition metals that can exhibit multi-valent states are very suitable. The rare earth elements are typically elements 58-71 of the periodic table, including Ce, Nd, etc. If an alkaline earth element (AE) were also present, the composition would be represented by the general formula RE-AE-TM-O."

And at page 7, lines 14-15, the specification states that "the rare earths site can also include alkaline earth elements."

The specification further states at page 11, lines 19-24, that "An example of a superconductive compound having a layer-type structure in accordance with the present invention is an oxide of the general composition  $RE_2TMO_4$ , where RE stands for the rare earths (lanthanides) or rare earth-like elements and TM stands for a transition metal."

The composition  $RE_2TMO_4:RE$  is referred to at page 24, lines 5-9;  $RE_{2-x}TM_xO_{4-y}$  is referred to at page 25, lines 19-21.

The following specific compounds are recited in the application:

$Ba_4La_{5-x}Cu_5O_{5(3-y)}$  at page 10, lines 4, 10, 14.

$La_{2-x}Ba_xCuO_{4-y}$  at page 12, line 13

$La_{2-x}Ba_xNiO_{4-y}$  at page 12, line 13

$La_{2-x}Sn_xNiO_{4-y}$  at page 12, line 17

$Ce_{2-x}Cu_xNiO_{4-y}$  at page 12, line 19

$La_2CuO_4$  at page 12, line 21

$La_2CuO_{4-y}$  with  $Sn^{2x}$  substitution at page 13, line 17

$Ba^{2x}$  and  $Ca^{2x}$

$\text{La}_{2-x}\text{Sn}_x\text{CuO}_{4-y}$  at page 17, line 21

$\text{La}_{2-x}\text{Ca}_x\text{CuO}_{4-y}$  at page 17, line 21

$\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$  at page 18, line 6

$\text{La}_2\text{CuO}_4:\text{Ba}$  at page 18, line 15

$\text{La}_2\text{CuO}_4:\text{Ba}$  at page 24, line 6

$\text{Nd}_2\text{NiO}_4:\text{Sn}$  at page 24, line 9

$\text{La}_2\text{CuO}_{4-y}$  doped with  $\text{Sn}^{2x}$ ,  $\text{Ca}^{2x}$  and  $\text{Ba}^{2x}$  at page 25, lines 6-18

Other compounds are given in the articles to B. Raveau, in Mat. Res. Bull., Vol. 20 (1985) pp. 667-671, and to C. Michel et al. in Rev. Claim. Min. 21 (1984) 407, both of which are incorporated by reference at page 13, lines 4-5.

The Examiner cites In re Fisher, 166 USPQ 18, In re Angstadt and Griffen, 150 USPO 214, and In re Golianni, 195 USPQ 150, in support of the statement "[t]he amount and type of examples necessary to support broad claims increases as the predictability of the art decreases".

The claims under appeal In re Fisher are directed to increasing the potency of substances containing ACTH hormones for injection into human beings. In regards to the rejection for insufficient disclosure under 35 USC 112 the CCPA states that:

"the issue thus presented is whether an inventor with the first to achieve potency of greater than 1.0 for certain types

of compositions, which potency was long designed because of its beneficial effects on humans, should be allowed to dominate *all* compositions having potencies greater 1.0, thus including future compositions having potencies in excess of those obtainable from his teachings plus ordinary skill." 166 USPQ 18, 23-24 (emphasis in the original).

The CCPA goes on to say in *In re Fisher* that:

"It is apparent that such an inventor should be allowed to dominate the future patentable inventions of others where those inventions were based in some way on his teachings. Such improvements, while unobvious from his teachings, are still within his contribution, since the improvement was made possible by his work. It is equally apparent, however, that he must not be committed to achieve this dominance by claims which are insufficiently supported and hence, not in compliance with the first paragraph of 35 USC 112. That paragraph requires that the scope of the claims must bear a reasonable correlation to the scope of enablement provided by the specification to persons of ordinary skills in the art... In cases involving unpredictable factors, such as most chemical reactions... the scope of enablement obviously varies inversely with the degree of unpredictability of the factors involved." (166 USPQ 18, 24)

Applicants of the present invention have provided the first teaching that transition metal oxides can form a superconductor having a critical temperature in excess of 26°K, therefore, "is apparent that such an [applicant] should be allowed to dominate the future patentable inventions of others when those inventions [are based in some way on applicants] teaching" as stated by the CCPA in *In re Fisher Supra*.

In the present invention Applicants are acknowledged to be the pioneers of high  $T_c$  superconducting metal oxides. The Examiner has produced no evidence that invention which come within the scope of Applicants' claim cannot be achieved by persons of skill in the art based on Applicants teaching. The affidavits of Mitzi, Dinger, Tsuei, Shaw and Duncombe and the book of Poole et al. state it is straight forward to use the general principles of ceramic science to make high  $T_c$  transition metal oxide superconductors following Applicants teaching.

The claimed invention in *re Angstadt and Griffen* (190 USPQ 214) involves a methods of catalyically oxidizing alkylaromatic hydrocarbons to form a reaction comprising the corresponding hydroperoxides. The method employs catalysts. The Examiner rejected all the claims under 35 USC 112, first and second paragraphs. The Board's rational for affirming the Examiner's rejection was directed primarily to the enablement required of the first paragraph.

The CCPA reversing stated that:

"what is a maximum concern in the analysis of whether a particular claim is supported by the disclosure in an application, is whether the disclosure contains sufficient teaching regarding the subject matter of the claims as enabled one of skill in the art to make and to use the claimed invention. These two requirements 'how to make' and 'how to use' have some times been referred to in combination as the 'enablement requirement'... The relevancy may be summed up as being whether the scope of enablement provided to one of ordinary skill in the art by the disclosure as such as to be commensurate with the scope or protection sought by the claims. (190 USPQ 214,47 citing In re Moore 169 USPQ).

In the attached affidavits under 37 CFR 132, Dr. T. Dinger, Dr. Tsuei, Dr. Shaw, Mr. Duncombe and Dr. D. Mitzi state:

"That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication, can make the transition metal oxide compositions encompassed by claims 24-26, 86-90 and 96-108, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art.

This is why the work of Bednorz and Müller was reproduced



so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery."

In the paragraph at the bottom of page 15 of the specification, it is stated that: in regard to compositions according to the present invention that "their manufacture generally follows the known principles of ceramic fabrication." Thereafter, an example of a typical manufacturing process is given.

The CCPA in *In re Angstadt and Griffen* further states that:

"we cannot agree with the Board that Appellants' disclosure is not sufficient to enable one of ordinary skill in the art to practice the invention without undue experimentation. We note that many chemical processes and catalytic processes particularly, are unpredictable, ... , and the scope of enablement varies inversely with the degree of unpredictability involved... The question, then, whether in an unpredictable art, section 112 requires the disclosure of a test with every species covered by a claim. To require such a complete disclosure will apparently necessitate a patent application or applications with 'thousands ' of examples... . More importantly, such a requirement would force an inventor to seek adequate patent protection to carry out a prohibited number of natural experiments. This would tend to discourage inventors in filing patent applications in an

unpredictable area since the patent claim would have to be limited those embodiments which are expressly disclosed. A potential infringer could readily avoid 'infringement of such claims' by merely finding another analogous (example) which could be used..." 190 USPQ 124, 218.

The CCPA in *In re Angstadt* further goes on to say

"having decided that appellants are *not* required to disclose every *species* encompassed by the claims even in an unpredictable art such as the present record presents, each case must be determined on its own facts." 190 USPQ 214, 218. (emphasis in the original).

In regards to the catalyst *In re Angstadt* and *Griffen* CCPA further states:

"since appellants have supplied the list of catalysts and have taught how to make or how to use them, we believe that the experimentation required to determine which catalyst will produce hydroperoxide would not be undue and certainly would not 'require ingenuity beyond that to be expected of one of ordinary skill in the art'. 190 USPQ, 214, 218 in *re Field v. Conover* 170 USPQ, 276, 279 (1971).

As stated in the affidavits of Dr. Dinger, Dr. Tsuei, Dr. Shaw, Mr. Duncombe and Dr. Mitzi, to make the high temperature superconductors encompassed by Applicants'

claims, using the teaching of the present invention would not require ingenuity beyond that expected of one of ordinary skill in the art.

The CCPA in *In re Angstadt* further states that:

"the basic policy of the Patent Act, which is to encourage disclosure of inventions and thereby to promote progress in the useful arts. To require disclosures in patent applications to transcend the level of knowledge of those skilled in the art would stifle the disclosure of inventions in fields man understands imperfectly." 190 USPQ 214, 219.

The CCPA further states that:

"the certainty which the law requires in patents is not greater than is reasonable." 242 USPQ, 270-271, cited in *In re Angstadt*. 190 USPQ 214, 219.

*In re Angstadt* further states at 190 USPQ 219:

We note that the PTO has the burden of giving reasons, supported by the record as a whole, why the specification is not enabling. *In re Armbruster*, 512 F.2d 676, 185 USPQ 152 (CCPA 1975). Showing that the disclosure entails undue experimentation is part of the PTO's initial burden under *Armbruster*; this court has never held that evidence is necessary for any experimentation, however slight, is sufficient to require

the applicant to prove that the type and amount of experimentation needed is not undue.

By calling the claimed "invention" the "scope of protection sought" the dissent obscures the problem and frustrates the intended operation of the patent system. Depriving inventors of claims which adequately protect them and limiting them to claims which practically invite appropriation of the invention which avoiding infringement inevitably has the effect of suppressing disclosure. What the dissent seem to be obsessed with is the thought of catalysts which won't work to produce the intended result. Applicants have enabled those in the art to see that this is a real possibility, which is commendable frankness in a disclosure. Without undue experimentation or effort or expense the combinations which do not work will readily be discovered and, of course, nobody will use them and the claims do not cover them. The dissent wants appellants to make everything predictable in advance, which is impracticable and unreasonable.

We hold that the evidence as a whole, including the inoperative as well as the operative examples, negates the PTO position that persons of ordinary skill in this art, given its unpredictability, must engage in undue experimentation to determine which complexes work. The key word is "undue," not "experimentation."

The only facts which the Examiner offers as evidence of unpredictability are examples provided in Applicants' specification. The CCPA in *In re Angstadt* says that this is "commendable frankness" which is not to be held against Applicants. The Examiner has provided no evidence that a person of skill in the art has to engage in undue experimentation to practice Applicants non-allowed claims. The affidavits of

Mitzi, Dinger, Tsuei, Shaw and Duncombe and the book of Poole et al. indicate that persons of skill in the art do not have to engage in undue experimentation to practice Applicants' invention.

The Examiner cited In re Colianni 195 USPQ 150 which applicants believe is not on point since in In re Colianni "[t]here is not a single specific example or embodiment by way of an illustration of how the claimed method is to be practiced." (195 USPQ 150, 152). In contradistinction as noted above, there are numerous examples cited in applicants' specification and incorporated references. Thus this decision is not on point.

"Showing that the disclosure entails undue experimentation is part of the PTO's initial burden." In re Armbruster 185 USPQ 152, 504.

"The practical approach followed consistently by [the CCPA] ..., places the initial burden on the PTO to show that the enabling disclosure is not commensurate in scope with the claim. Upon such a showing, the burden of rebuttal shifts to applicants". In re Coliani 195 USPQ 150.

"However, [the CCPA] has made it clear that the Patent and Trademark Office must substantiate its rejections for lack of enablement with reasons" In re Armbruster 185 USPQ 152, 153.

The Examiner has merely asserted without support that "the art of high temperature superconductivity is unpredictable...".

The CCPA in *In re Marzocchi*, 58 CCPA 1069, 439 F. 2d 220, 169 USPQ 367, 369-370 (1971) states:

"The only relevant concern of the Patent Office under these circumstances should be over the *truth* of any such assertion. The first paragraph of §112 requires nothing more than objective enablement. How such a teaching is set forth, either by the use of illustrative examples or by broad terminology, is of no importance.

As a matter of Patent Office practice, then, a specification disclosure which contains a teaching of the manner and process of making and using the invention in terms which correspond in scope to those used in describing and defining the subject matter sought to be patented *must* be taken as in compliance with the enabling requirement of the first paragraph of §112 *unless* there is reason to doubt the objective truth of the statements contained therein which must be relied on for enabling support. Assuming that sufficient reason for such doubt does exist, a rejection for failure to teach how to make and/or use will be proper on that basis; such a rejection can be overcome by suitable proofs indicating that the teaching contained in the specification is truly enabling...

[I]t is incumbent upon the Patent Office, whenever a rejection on this basis is made, to explain *why* it doubts the truth or accuracy of any statement in a supporting disclosure and to back up assertions of its own with acceptable evidence or reasoning which is inconsistent with the contested statement. Otherwise, there would be no need for the applicant to go to the trouble and expense of supporting his presumptively accurate disclosure. [Emphasis in original footnote deleted].

Applicants have enclosed herewith affidavits of Dr. Mitzi, Dr. Tsuei, Dr. Shaw, Mr. Duncombe and Dr. Dinger under 37 CFR 132 which state, as quoted above, that once a person of skill in the art knows of applicants' work, the compositions encompassed by the claims under experimentation, can be made using the teaching of applicants without undue experimentation.

Thereby rebutting the Examiner's statement that:

"[the specification ... [fails] to provide an enabling disclosure commensurate with the scope of the claims."

ee@@

The Examiner cites *In re Cooks and Cosden Oil v. American Hoechst* to support the statement "[c]laims broad enough to cover a large number of compositions that do not exhibit the desired properties fail to satisfy the requirement of 35 USC 112."

Applicants claims do not read on any inoperative specifies since Applicants' claims are method of use claims. A composition which does not have a  $T_c > 26^\circ\text{K}$  is not within the scope of the claims. Thus these decisions are not on point.

The Examiner cites In re Corkill as support for this statement "[m]erely reciting a desired result does not overcome this failure". The CAFC held "[c]laims which include a substantial measure of inoperatives ... are fairly rejected under 35 USC 112."

Applicants' claims include no inoperatives. Since Applicants claims are method of use claims they are functional and thus exclude inoperatives. "[T]he use of functional language is sanctioned specifically by ... section 112." In re Angstadt 190 USPQ 214, 217.

The Examiner cited Brenner v. Manson for the statement "a patent is not a hunting license. It is not a reward for the search, but a reward for its successful conclusion." The claim in question was a method of making a composition. The composition had no known use. The method was found to lack utility and thus is not be patentable. This is not relevant to §112, first paragraph. Thus this decision is not on point. Moreover, Applicants have had a successful conclusion, they won a Nobell Prize and initiated and enabled the high  $T_c$  transition metal oxide art.

The Examiner queries "[w]ill any layered perovskite material containing copper exhibit superconductivity?" and "does any stoichiometric combination of rare earth, an alkaline earth, and copper elements result in an oxide superconductor?" Since applicants claims are directed to methods of using oxide compositions, applicants'



claims read on only those layered perovskite materials which exhibit superconductivity with a  $T_c > 26 \text{ }^\circ\text{K}$  and do not read on methods of use of oxide compositions which are not superconductive. Thus the Examiner's queries is not relevant to applicants claims. Applicants are not claiming a composition which is a high  $T_c$  superconductor. Thus applicants claims do not read on any layer perovskite, or any other stoichiometric combination, but only those carrying a high  $T_c$  superconducting current. Method of use claims are inherently narrower in scope than composition claims.

The paragraph bridging pages 13 and 14 refer to Ba-La-Cu-O systems having different crystallographic phases having  $\text{Cu}^{3+}$  and  $\text{Cu}^{2+}$  ions or  $\text{Ni}^{3+}$  and  $\text{Ni}_2^{+}$  ions.

Claim 103 of the present invention recites "a copper oxide compound having a layer-type-perovskite-like crystal structure, the copper oxide compound including at least one rare-earth or rare-earth-like element, and at least one alkaline-earth element". In regard to the stated elements, the rare earth elements are defined in the specification at page 7, lines 9-12 to be "a group IIIB element, such as La." Group IIIB includes Sc, Y, La and Ac, rare earth-like or near rare earth. The rare earth elements are elements 58 to 71. This group contains four elements from group IIIB and fourteen elements from the rare-earth for a total of 18 elements. The alkaline earths contain the elements of Group A which has 6 elements.

The Examiner further states:

It should be noted that at the time the invention was made, the theoretical mechanism of superconductivity in these materials was not well understood. That mechanism still is not understood. Accordingly, there appears to be little factual or theoretical basis for extending the scope of the claims much beyond the proportions and materials actually demonstrated to exhibit high temperature superconductivity. A "patent is not a hunting license. It is not a reward for the search, but a reward for its successful conclusion".

The Examiner has provided no evidence to support the statement "that at the time the invention was made, the theoretical mechanism of superconductivity in these materials was not well understood. That mechanism is still not understood." Applicants request the Examiner to introduce evidence to support this statement or to place an Examiner's affidavit under MPEP 706.02(a) qualifying the Examiner as an expert to make this statement. The Examiner further states "there appears to be little factual or theoretical basis for extending the scope of the claims much beyond the proportions and materials actually demonstrated to exhibit high temperature superconductivity." This is the Examiner's unsupported opinion. The five affidavits of Mitzi, Dinger, Tsuei, Shaw and Duncombe under 37 CFR 1.132 and the book to Poole et al. described below provide factual evidence supporting Applicants position that once a person of skill in the art knew from Applicant's article that transition metal oxides were high T<sub>c</sub> superconductors, it was a matter of routine application of the general principles of

ceramic science to fabricate transition metal oxide superconductors other than those actually made by applicants. Quoting "Brenner v. Manson", 283 US 518, 148 USPQ 689, the Examiner further states that a "patent is not a hunting license. It is not a reward for the search, but a reward for its successful conclusion." The evidence introduced by Applicants clearly shows that Applicant's article upon which the present application is based had a very successful conclusion. Applicants started the field of high Tc superconductivity. All the further developments were based on Applicants teaching. Moreover, the issue in Brenner v. Manson was the patentability of a method to fabricate a composition. The composition had no use. The method was found not patentable for lack of utility. To issue a patent for such a process would be granting a hunting license for a utility that may occur in the future. This case has nothing to do with §112 enablement.

In view of the above Applicants request the Board to reverse the Examiner's objection to the specification.

## **CLAIM REJECTIONS UNDER 35 USC §112, FIRST PARAGRAPH**

Claims 24-26, 86-90, 96-113, 129-131, 134, 135, and 139-177 are rejected under 35 U.S.C. § 112, first paragraph, for the same reasons set forth by the Examiner in the objection to the specification. Applicants disagree for the same reasons why Applicants disagreed to the objection to the specification above. The Examiner provides specific comments only in regards to claims 24, 86, 88, 96 and 103.

Applicants disagree with the Examiner's statement that Applicants' arguments filed April 11, 1996, January 3, 1996, and September 29, 1995, paper nos. 53, 50, and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996, paper nos. 49 and 52, have been fully considered but they are not deemed to be persuasive. The arguments of those papers are incorporated herein by reference.

The Examiner further states:

"The additional case law and arguments by the applicants have been duly noted. For the reasons that follow, however, the record as a whole is deemed to support the initial determination that the originally filed disclosure would not have enabled one skilled in the art to make and use the invention to the scope that it is presently claimed."

The Examiner again uses the word "deemed", that is, it is the Examiner's opinion unsupported by any factual evidence. The quoted passage is completely contrary to the Examiner's rejection under 35 USC 102(a) and 103(a). Under these rejections the Examiner found the Asahi Shinbum article would have enabled one skilled in the art to make and use the invention to the scope that it is presently claimed. As noted above, the Asahi Shinbum article relies upon Applicants article. Applicants' view is further supported by the five affidavits of Mitzi, Tsuei, Dinger, Shaw and Duncombe under 37 CFR 1.132 and the book of Poole which will be described below and which states that once it was known from Applicants article that transition metal oxides were superconductive at temperatures above 26°K, other high Tc transition metal oxides could be made by a person of skill in the art using the teaching of Applicants and the general teachings of ceramic science.

The Examiner further states:

ii. The applicants quote several passages from their specification at pp. 13-15 of their September 29, 1995 Amendment, but the issue is the scope of enablement, not support. The present disclosure may or may not provide support for particular embodiments, but the issue here is the scope to which that disclosure would have taught one skilled in the art how to make and use a composition which shows the onset of superconductivity at above 26°K.

Applicants are not required to provide experimental evidence for every species within the scope of their claims. The entire filed of high  $T_c$  superconductivity is based on Applicants' work, in particular, on Applicants' article. This affidavit of James W. Leonard under 37 CFR 1.132 submitted on December 15, 1998 states that 5,689 articles cited Applicants' article (Z. FurPhys. B, 64, pp. 185-193 (September 1986)). This is clear evidence that Applicant article originated and enabled the filed of high  $T_c$  superconductivity. It is clear by the facts presented by Applicants that they "have taught one of skill in the art how to make and use a composition which shows the onset of superconductivity at above 26°K". The Examiner has introduced no factual evidence to the contrary. The Examiner merely "deems" that Applicants' claims are not enabled.

The Examiner further states:

- iii. Construed in light of that issue, the invention is not deemed to have been fully enabled by the disclosure to the extent presently claimed.

The Examiner again "deems" Applicants claims not enabled without factual support.

The Examiner further states:

- (1) In their September 29, 1995 Amendment, the applicants argue that their disclosure refers to "the composition represented by the formula RE-TM-0, where RE is a rare earth or rare earth-like element, TM is a

nonmagnetic transition metal, and O is oxygen", and list several species such as "**La<sub>2-x</sub>Ba<sub>x</sub>CuO<sub>4-y</sub>**" which they indicate are found in the present disclosure.

Applicants disagree. The passages quoted in the September 29, 1995 amendment lists numerous specific compositions and generic formula as indicated above. The listed species were preferred embodiments at the time of filing the present application. Preferred embodiments do not provide a limitation to the broad scope of applicants teaching.

The Examiner further states:

(2) Notwithstanding that argument, it still does not follow that the invention is fully enabled for the scope presently claimed. The claims include formulae which are much broader than the RE-TM-0 formula cited in the disclosure. Claim 24 recites "a transition metal oxide", claim 88 "a composition", and claim 96 "a copper-oxide compound".

As noted above the specification at page 1, line 5-10, states "[t]his invention relates to ... superconducting compositions including copper and/or transition metals." And at page 5, lines 5-9 "[i]t is [an] ... object of the present invention ... to provide novel superconductive compositions that are oxides."

The Examiner further states:

(a) The present specification actually shows that known forms of "a transition metal oxide", "a composition", and "a copper-oxide compound" do not show the onset of superconductivity at above 26°K. At p. 3, line 20, through p. 4, line 9, of their disclosure, the applicants state that the prior art includes a "Li-Ti-O system with superconducting onsets as high as 13.7°K. " Official Notice is taken of the well-known fact that Ti is a transition metal. That disclosure also refers to "a second, non-conducting CuO phase" at p. 14, line 18.

Applicants claims are directed to "transition metal oxides", "a composition" and "a copper-oxide compound" having a  $T_c$  in excess of 26°K which is carrying a superconducting current. Applicants claims do not include in the claimed method compositions having  $T_c < 26^\circ\text{K}$ . Thus the examples on page 3, line 20 - page 4, line 9, are not included in applicants claims. That these are transition metal oxides having  $T_c < 26^\circ\text{K}$  does not mean that Applicants' claims directed to transition metal oxides, compositions and copper oxides having  $T_c > 26^\circ\text{K}$  are not enabled. Applicants provide the teaching on how to fabricate such oxides having  $T_c > 26^\circ\text{K}$ . The "second non-conducting CuO phase" referred to at page 14, line 18, again does not mean that applicants claims are not enabled. Applicants statements at page 14 is part of applicants teaching on how to achieve an oxide having a  $T_c > 26^\circ\text{K}$ . The Examiner is attempting to use Applicants complete description of their teaching to show lack of



enablement when, in fact, this complete teaching provides full enablement by showing how samples are and are not to be prepared. Applicants have claimed their invention functionally, that is, as a method of use so the Applicants' claim do not read on inoperable species. What the Examiner "seems to be obsessed with is the thought of [transition metal oxides] which won't work to produce the intended result. Applicants have enabled those of skill in the art to see that this is a real possibility which is commendable frankness in a disclosure." In re Angstadt, Supra.

The Examiner further states:

(b) Accordingly, the present disclosure is not deemed to have been fully enabling with respect to the "transition metal oxide" of claim 24, the "composition" of claim 88, or the "copper-oxide compound" of claim 96.

Again without facts the Examiner "deems" Applicants' claims not enabled and for the reasons given above applicants disagree. The only attempt at a factual support for the Examiner's statement are the examples provided by Applicants which show  $T_c < 26^\circ\text{K}$ . Applicants provide this teaching so that a person of skill in the art will be fully informed on how to practice Applicants invention.

The Examiner further states:

(3) The examples at p. 18, lines 1-20, of the present specification further substantiates the finding that the invention is not fully enabled for the scope presently claimed.

(a) With a 1:1 ratio of (Ba, La) to Cu and an x value of 0.02, the La-Ba-Cu-O form (i.e., "RE-AE-TM-0", per p. 8, line 11) shows "no superconductivity".

This part of Applicants' teaching providing a complete teaching which permits a person of skill in the art to be fully enabled to practice Applicants' claimed invention. The issue according to *In re Angstadt* (referred to above) is whether Applicants have enabled those of skill in the art to practice Applicants invention without undue experimentation. That a person of skill in the art has to do experimentation to determine suitable combinations of elements to form a composition having  $T_c > 26^\circ\text{K}$  through which a superconductive current flows is not an indication of a lack of enablement. Thus Applicants cited examples of compositions having  $T_c < 26^\circ\text{K}$  does not show lack of enablement.

The Examiner further states in regards to the examples at p. 18, lines 1-20:

(b) With a 2:1 ratio of (Ba, La) to Cu and an x value of 0.15, the La-Ba-Cu-O form shows an onset of superconductivity at " $T_c = 26^\circ\text{K}$ ". It should be noted, however, that all of the claims in this application require

the critical temperature ( $T_c$ ) to be "in excess of  $26^\circ\text{K}$ " or "greater than  $26^\circ\text{K}$ ".

Applicants do not believe that an on set of a  $T_c$  at  $26^\circ\text{K}$  is different than and greater than  $26^\circ\text{K}$ . Greater than  $26^\circ\text{K}$  can mean  $T_c = 26^\circ\text{K}$  plus some infinitesimal temperature.

The Examiner further states:

(c) Consequently, the present disclosure is not deemed to adequately enable the full scope of the present claims. Independent claims 86 and 103 may require the presence of rare earth, alkaline earth, and transition metals, but the aforementioned examples show that superconductivity is still very unpredictable. Those claims cannot be deemed to be fully enabled.

The Examiner again "deems" claims 86 and 103 as not fully enabled. This again is the Examiner's opinion. Claims 86 and 103 do not read on the examples cited in Applicants' specification which are superconductors having  $T_c < 26^\circ\text{K}$ . Thus these examples are not evidence that claims 86 and 103 are not enabled. The examples are part of the teaching enabling a person of skill in the art to practice the invention of claims 86 and 103.

The Examiner further states:

iv. The applicants also have submitted [five] affidavits attesting to the applicants' status as the discoverers of materials that superconduct > 26°K. Each of the affidavits further states that "all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar manner (way)". Each of the affidavits add "(t)hat once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the (present) application, which includes all known principles of ceramic fabrication, can make the transition metal oxide compositions encompassed by (the present) claims ... without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art."

Applicants acknowledge that all five affiants are the employees of the assignee of the present application. (The affidavit of Shaw and Duncombe were submitted after the date of the final rejection and were considered as indicated by the Advisory Action dated February 25, 1999).

The Examiner states in response to the affidavits of Mitzi, Tsuei and Dinger:

(1) Those affidavits do not set forth particular facts to support the conclusions that all superconductors based on the applicants' work behave in the same way and that one skilled in the art can make those superconductors without undue experimentation. Conclusory statements in an affidavit or specification do not provide the factual evidence needed for patentability.

The Examiner cited *In re Lindner*, 173 USPQ 356, 358 (CCPA 1972) in support of this statement. In *In re Lindner* the patent applicant submitted Rule 132 affidavit based on one example to show unexpected results for a claim of broader scope. The CCPA held that "[i]t is well established that objective evidence of non-obviousness must be commensurate in scope with the claims." *In re Lindner* is not on point since it does not deal with the issue of enablement. A single example can enable a broader scope claim where nothing more is needed than what is taught by Applicants or what is taught by Applicants together with what is known by a person of skill in the art.

The affidavits of Mitzi, Tsuei, Dinger, Shaw and Duncombe are statements of experts in the ceramic arts. The Examiner disagrees with these experts. But the Examiner has not submitted an Examiner's affidavit qualifying himself as an expert to rebut the statements of Applicants' affidavits.

The Examiner further states:

(2) Those affidavits do not overcome the non-enablement rejection.

The present specification discloses on its face that only certain oxide compositions of rare earth, alkaline earth, and transition metals made according to certain steps will superconduct at  $>26^{\circ}\text{K}$ .

Applicants disagree. The affidavits of Shaw and Duncombe cites numerous books and articles which provide the general teaching of ceramic science at the time of and prior to the filing date of the present application. The affidavit of Duncombe also provides several hundred pages copied from Mr. Duncombe's notebooks starting from before Applicants' filing date. In regards to these pages, Mr. Duncombe states "I have recorded research notes relating to superconductor oxide (perovskite) compounds in technical notebook IV with entries from November 12, 1987 to June 14, 1988 and in technical notebook V with entries continuing from June 7, 1988 to May 1989." Mr. Duncombe's affidavit list some of the compounds prepared using the general principles of ceramic science:  $\text{Y}_1 \text{Ba}_2 \text{Cu}_3 \text{O}_x$ ,

$\text{Y}_1 \text{Ba}_2 \text{Cu}_3 \text{O}_3$ ,  $\text{Bi}_{2.15} \text{Sr}_{1.98} \text{Ca}_{1.7} \text{Cu}_2 \text{O}_{8+8}$ ,  $\text{Ca}_{(2-x)} \text{Sr}_x \text{Cu O}_x$  and  $\text{Bi}_2 \text{Sr}_2 \text{Cu O}_x$ .

The Examiner further states:

(3) Those affidavits are not deemed to shed light on the state of the art and enablement at the time the invention was made. One may know now of a material that superconducts at more than  $26^{\circ}\text{K}$ , but the affidavits do not establish the existence of that knowledge on the filing date for the

present application. Even if the present application "includes all known principles of ceramic fabrication", those affidavits do not establish the level of skill in the ceramic art as of the filing date of that application.

The Examiner states that "these affidavits are not **deemed** to shed light on the state of the art and enablement at the time the invention was made," that is, it is the Examiner's opinion. Applicants disagree. The affidavits clearly state that all that is needed is Applicants' teaching and the ordinary skill of the art to practice applicants claimed invention. Also, 35 USC §112, does not require that enablement be determined "at the time the invention was made". This language appears in 35 USC §103, but not in 35 USC §112. Thus it is clear that it was not the intent of Congress to determine enablement at the time the invention was made in the manner suggested by the Examiner. All that is necessary is "[t]he specification shall contain a written description ... to enable any person skilled in the art ... to make and use the same." Applicants initiated the filed of high  $T_c$  superconductors. If a person of skill in the art from the description in Applicants' specification can practice applicants' claimed invention, it is enabled. Applicants' are not required to show that a person of skill in the art had the knowledge prior to Applicants' invention. If this were the case Applicants would not be the first, sole and only inventors, since the invention would be known by others. Applicants teach ceramic processing methods to fabricate high  $T_c$  superconductors. This uses general principles of ceramic science known prior to the filing date of the present application. Thus applicants' claims are fully enabled. The Examiner has provided no evidence to the contrary. The Examiner has produced no

evidence to demonstrate that a person of skill in the art, at the time of applicants filing date, could not practice the claimed invention from Applicants teaching. The utilization of such teaching to practice Applicants' claimed invention was not known prior to Applicants' filing date. That is Applicants' discovery and thus why they are entitled to their claimed invention.

The Examiner further states:

(4) It is fully understood that the applicants are the pioneers in high temperature metal oxide superconductivity. The finding remains, nonetheless, that the disclosure, is not fully enabling for the scope of the present claims.

If Applicants pioneered the field of high  $T_c$  superconductivity, that is, they initiated the substantial worldwide effort to validate their discovery and to synthesize others specific embodiment of their generic and specific teaching, then applicants should be entitled to generic claims since other based their work on applicants' teaching.

The Examiner has cited the following seven decisions, which have been discussed in detail below, in support for the determination of non-enablement: In re Fisher, 166 USPQ 18, 24; and In re Angstadt and Griffen, 190 USPQ 214, 218. In re Colianni, 195 USPQ 150, 153, 154 (CCPA 1977). In re Cook, 169 USPQ 298, 302; and



Cosden Oil v. American Hoechst, 214 USPQ 244, 262. In re Corkill, 226 USPQ 105, 1009. Brenner v. Manson, 383 US 519, 148 USPQ 689.

The Examiner has not applied the rational of these decisions. In fact, in the prosecution Applicant pointed out that the Examiner seems to have specifically avoided applying this case law and, consequently, applicants take the Examiner's silence as concurrence in the manner that applicants have applied this case law. In response to this the Examiner states "[n]otwithstanding the applicants' commentary on caselaw, the April 15, 1997 Office Action, paper no. 54, sets forth the factual basis for the determination of non-enablement at pp. 5-10." It is applicants view that the Examiner is misapplying this case law.

In this regard the Examiner further states:

(3) The applicants still further argues "that the Examiner does not rebut the case law and argument provided by applicants on (pages) 15-25 of their September 29, 1995 amendment which addresses (these issues) in detail." The point remains, nevertheless, that there appears to be a concurrence as to the applicable caselaw. That caselaw speaks for itself What has been fully addressed in the previous Office Action and repeated above is the factual basis for the determination of non-enablement for the scope of the present invention.

Case law does not speak for itself. The rule of a case depends on the facts of the case. The fact circumstances in the case must be compared with those of the present application to justify application of the decision of the case. The Examiner has not done this. Applicants have shown above that the case law when properly applied support Applicants' position that their claims are enabled and does not support the Examiner's position that the non-allowed claims are not enabled.

The Examiner states:

ii. The applicants urge that "their disclosure supports a substantially broader scope than (particular) species." With respect to transition metals, the applicants point to the support in their disclosure and argue that they were enabled for transition metals other than just copper. Again, however, it is noted that high temperature superconductivity is a highly unpredictable art. In view of the record as a whole, it is again determined that one skilled in the art would not have been enabled to practice the presently disclosed invention with transition metals other than copper.

"The first paragraph of §112 requires nothing more than objective enablement , how such teaching is set forth , either by the use of illustrative examples or by broad terminology is of no importance" In re Marzochi, Supra. The Examiner has provided no factual evidence to support the Examiner's statement that the field of high  $T_c$  superconductivity is unpredictable. The Examiner has attempted to support this

position based on Applicants' teaching. That teaching is part of Applicants' enabling disclosure. In the last sentence of the passage above the Examiner implies that applicants claims directed to copper are enabled. Applicants teach transition metals. Copper is a transition metal. Applicants teaching enable persons of skill in the art to make transition metal oxides which sustain a superconducting current at  $T_c > 26^\circ\text{K}$ . The Examiner has provided no factual evidence that Applicants claims are not enabled for transition metals.

The Examiner states:

iii. The applicants argue that their own examples do not support the determination of non-enabling scope of the invention. Nevertheless, the record is viewed as a whole. If the applicants could not show superconductivity with a  $T_c > 26^\circ\text{K}$  for certain compositions falling within the scope of the present claims, it is unclear how someone else skilled in the art would have been enabled to do so at the time the invention was made.

The Examiner incorrectly states "applicants could not show superconductivity with  $T_c > 26^\circ\text{K}$  for certain compositions falling within the scope of the present claims." The present claims are directed to a method of flowing a superconducting current in a composition having a  $T_c > 26^\circ\text{K}$ . If a composition has a  $T_c < 26^\circ\text{K}$ , a method of flowing a superconducting current in such a compound cannot fall within the scope of

applicants claims. Applicants are not claiming a composition of matter. They are claiming their discovery, passing a superconductive current through a transition metal oxide having a  $T_c > 26^\circ\text{K}$ . No one prior to applicants knew this. That is why they received the Nobel Prize in Physics in 1987.

The Examiner further states that Applicants' affidavits are conclusory. The Examiner appears to be placing himself up as an expert in the field of superconductivity. Applicants requested that the Examiner submit an affidavit in the present application rebutting the position taken by applicants' five affiants, but the Examiner has not submitted an affidavit. The facts are that the five affiants are experts in the art, the Examiner is not. The Examiner states that those "affidavits were insufficient because they were conclusory only, i.e., they lacked particular facts to support the conclusions reached". Applicants submitted the affidavit of Peter Duncombe which has provided hundreds of pages of notebook entries showing that he fabricated superconductive transition metal oxides according to the teaching of applicants specification.

The Examiner has provided no substantial evidence to support this assertion of non-enabling scope of the invention. It is requested that the Examiner support his assertion with factual evidence and not unsupported statements.

The Examiner is applying an incorrect standard of enablement. The Examiner is applying a standard applicable to composition of matter. Applicants are not claiming a

composition of matter. As shown by applicants prior comments applicants have in fact fully enabled the composition of matter. Therefore, applicants have provided excess enablement for the claimed invention. The standard of enablement for a method of use is not the same as the standard of enablement for a composition of a matter.

Notwithstanding, it is well settled law that claims to a composition of matter can encompass a number of inoperable species. However, Applicants' claims do not cover any inoperable species. The claims only encompass methods of flowing a superconducting current in transition metal oxides that are superconducting at temperatures in excess of 26°K. Those transition metal oxides that are not superconducting at temperatures in excess of 26°K are not encompassed by applicants claims reciting these limitations. Applicants note that a claim to a composition of matter is dominant to any use of that composition of matter and claims directed to a method of use of a composition of matter are necessarily of narrower scope than claims to the composition of matter. Applicants' claims do not encompass uses other than those which the claims are limited to by the use limitations recited in the claims. Applicants' claims are directed to what they have discovered. Therefore, applicants' claims fully satisfy the requirements of 35 USC 112.

The claimed invention is enabling because it is directed to a method of use rather than a composition. Applicants are claiming their discovery, showing superconducting current in a transition metal oxides with a  $T_c > 26^\circ\text{K}$ . If a patent applicant claims a method of flowing current through a circuit having a resistive element, the applicant does not have to describe every method of making every type of

resistive element for the claim to dominate all resistive elements. Such a claim reads on resistive elements made of materials not known at the time of filing since the discovery is not the material but the method of use. Applicants discovered that a superconducting current can be flowed in a transition metal oxides having a  $T_c > 26^\circ\text{K}$ . That is what applicants are claiming.

Process of use claims are subject to the statutory provisions of 35 USC 112, first paragraph. All that is necessary to satisfy §112 is the statement that a superconducting current can be passed through a transition metal oxides having a  $T_c > 26^\circ\text{K}$ . The Examiner has essentially said this by rejecting applicants non-allowed claims as anticipated under §102(a) or obvious under §103(a) in view of the Asahi Shinbum article. Applicants only allowed claim 136 was allowed over the Asahi Shinbum article because it showed criticality for the formula recited in claim 136. Since Applicants generic teaching does not prevent others from obtaining patents to specific formulas, Applicants are entitled to generic claims to their discovery. Applicants filed this application soon after their discovery. Applicants availed themselves of the one year grace period under 35 USC 102(b) by publishing their results before filing the present application. This was the quickest way to promote the progress of the field of high  $T_c$  superconductivity which can have substantial societal benefits such as less expensive electric power and more effective medical diagnostic tools. It is a policy of the United States Constitution, which establishes the United States Patent System, to encourage early disclosure of inventions to promote the progress of the useful arts. The Examiner's position that Applicants generic claims are not fully enabled frustrates this

policy. Applicants could have decided not to publish Applicants' article and not to file the present application while engaging in years of further experimentation to find all specific examples which had the optimal  $T_c$ . If Applicants acted this way, there would not have been the explosive worldwide effort to fully explore and implement high  $T_c$  transition metal oxide technology. The rationale used by the Examiner is contrary to the Constitutional policy to promote the progress of the useful arts by early disclosure of an invention. Early disclosure should not be a penalty to Applicants. Applicants are pioneers in discovering that transition metal oxides have  $T_c > 26^\circ\text{K}$ . A first discoverer of a wheel whose specific embodiment is a solid disc rotateable about an axle can claim a cylindrical member adapted for rotation about the axle and for rolling on a surface, that is, their discovery. This claim is dominant to a latter inventor's improved wheel comprising spokes which has the advantage of much lighter weight than a disc. The latter inventor is entitled to subservient claim to the dominant claim to a wheel. Applicants are entitled to a dominant claim to their discovery.

The Examiner has not shown by evidence not contained within applicants' teaching that the art of high  $T_c$  superconductors is unpredictable. The Examiner has attempted to use applicants' teaching to establish such unpredictability. The Examiner has essentially not responded to Applicants' comments. The Examiner has introduced no extrinsic evidence to support the Examiner's opinion that the field of high  $T_c$  superconductivity is unpredictable. The Examiner has not introduced an affidavit qualifying himself to offer such an opinion. The Examiner merely states that his opinion is supported by the record as a whole. The only thing that Examiner relies on is some

examples referred to above which do not have  $T_c > 26^\circ\text{K}$  which as stated above is part of Applicants' enabling disclosure.

In response to the resubmitted 1.132 Affidavits of Mitzi, Tsuei and Dinger (filed 12/16/98) and the newly provided 1.132 Affidavits of Thomas Shaw (filed 12/16/98) and Peter Duncombe (filed 12/21/98) the Examiner states:

The Examiner notes the books describing the general principles of ceramic fabrication provided in these Affidavits. Also, the examiner notes that such fabrication techniques were utilized subsequently (after the filing date of the instant application) to produce the superconductive materials described in the Poole et al reference as well as the materials produced by Peter Duncombe (see Affidavit filed 12/21/98).

The affidavit of Peter Duncombe provides notebook entries beginning November 12, 1987, which is prior to Applicants filing date and prior to the Asahi Shinbum article. Duncombe used the general principles of ceramic science to implement the invention described in Applicants article. Each of the five affiants Tsuei, Mitzi, Duncombe, Shaw and Dinger are experts in the field of ceramics. Each has stated the Applicants' claimed invention can be implemented based on Applicants teaching and with nothing more than the general principles of ceramic science known at the time of filing of the present application.



The Examiner states:

It is the examiner's maintained position that while general principles of ceramic fabrication were most certainly known prior to the filing date of the instant application, the utilization of such techniques to produce superconductive materials within the scope of the instant claims were not known. The affidavits are not effective to demonstrate enablement at the time of the invention was made. As stated in paper #66, page 8, one may now know of a material that superconduct at more than 26K, but the affidavits do not establish the existence of that knowledge on the filing date of the present application.

The Examiner acknowledges that the fabrication techniques necessary to practice Applicants' invention were known prior to the filing dated of the present application. But the Examiner further states that the "utilization of such techniques to produce superconductive materials within the scope of the instant claims were not known". The scope of the instant claim is flowing a superconductive current in a transition metal oxide having a  $T_c > 26^\circ\text{K}$ . That is Applicants' discovery. That is why it was not known prior to Applicants' discovery. How to make this type of material was known. Prior to Applicants' discovery, It was not known that they were superconductive with a  $T_c > 26^\circ\text{K}$ . The Examiner incorrectly states "one may now learn of a material that superconducts at more than 26°K, but the affidavits do not establish the existence of that knowledge on the filing date of the present invention." If that knowledge was

known by another prior to the filing date, Applicants would not have a patentable invention since they would not be the initial first and sole inventor. The affidavits state that the knowledge of how to make transition metal oxides by the general principles of ceramic science were known prior to the filing date. In particular, the affidavits of Duncombe and Shaw refer to a number of articles and texts on the general principles of ceramic science. One of these texts is "Structures, Properties and Preparation of Perovskite-type Compounds", F.S. Galasso (1969).

Applicants note that the book "Copper Oxide Superconductors" by Charles P. Poole, Jr., Timir Datta and Horacio A. Farach, John Wiley & Sons (1998) support their position that high temperature superconductors were not difficult to make after their original discovery. This book shall be referred to herein as Poole et al. or the Poole book. The Poole book was published after Applicants' initial discovery which was published in Applicants' article. The Examiner states "[a]s such, it does not, provide evidence of the state of the art at the time the presently claimed invention was made".

Applicants disagree. The preface of this book says "[t]his volume reviews the experimental aspects of the field of oxide superconductivity with transition temperatures from 30K to above 123K, from the time of its discovery by Bednorz and Muller in April, 1986 until a few months after the award of the Nobel Prize to them in October, 1987." Thus the book reports on work done within eighteen months of Applicants' discovery in April 1986 and within eleven months of its publication in September, 1986. In the present application was filed on May 22, 1987. This passage is referring to Applicants

and Applicants' article referred to at page 6 of Applicants' specification. This book acknowledges that applicants are the discoverers of the field of high temperature superconductivity. (See Attachment A of Applicants' response dated May 14, 1998 and See Attachment H of Applicants' response dated November 28, 1997). The Examiner's view that the skill of the art was insufficient at the time of the filing date of the present application is untenable in the view of Poole et al. and Applicants' 132 affidavits of Tsuei, Mitzi, Shaw, Dinger and Duncombe, in particular that of Peter Duncombe which reports data prior to the Applicants' filing date.

Applicants note that it is generally recognized that it is not difficult to fabricate transition metal oxides and in particular copper metal oxides that are superconductive after the discovery by applicants that transition metal oxides are high  $T_c$  superconductors. Chapter 5 of the Poole et al. book entitled "Preparation and Characterization of Samples" states at page 59 "[c]opper oxide superconductors with a purity sufficient to exhibit zero resistivity or to demonstrate levitation (Early) are not difficult to synthesize. We believe that this is at least partially responsible for the explosive worldwide growth in these materials". Poole et al. further states at page 61 "[i]n this section three methods of preparation will be described, namely, the solid state, the coprecipitation, and the sol-gel techniques (Hatfi). The widely used solid-state technique permits off-the-shelf chemicals to be directly calcined into superconductors, and it requires little familiarity with the subtle physicochemical process involved in the transformation of a mixture of compounds into a superconductor." Poole et al. further states at pages 61-62 "[i]n the solid state reaction technique one starts with oxygen-rich

compounds of the desired components such as oxides, nitrates or carbonates of Ba, Bi, La, Sr, Ti, Y or other elements. ... These compounds are mixed in the desired atomic ratios and ground to a fine powder to facilitate the calcination process. Then these room-temperature-stable salts are reacted by calcination for an extended period (~20hr) at elevated temperatures (~900°C). This process may be repeated several times, with pulverizing and mixing of the partially calcined material at each step." This is generally the same as the specific examples provided by applicants and as generally described at pages 8, line 19, to page 9, line 5, of Applicants' specification which states "[t]he methods by which these superconductive compositions can be made can use known principals of ceramic fabrication, including the mixing of powders containing the rare earth or rare earth-like, alkaline earth, and transition metal elements, coprecipitation of these materials, and heating steps in oxygen or air. A particularly suitable superconducting material in accordance with this invention is one containing copper as the transition metal." (See Attachment A of Applicants' response dated May 14, 1998 and See Attachment H of Applicants' response dated November 28, 1997). Consequently, applicants have fully enabled high T<sub>c</sub> transition metal oxides and their claims.

As stated in the affidavit of Dr. Mitzi, Dr. Dinger, Dr. Tsuei, Dr. Shaw and Mr. Doncombe the preface of the book by Poole et al., quoted above, the work of Applicants initiated the field of high temperature superconductors and these materials are not difficult to synthesize. And according to Fisher "it is apparent that such an

inventor should be allowed to dominate future patentable inventions of others where those inventions were based in some way on his teaching." (166 USPQ 18, 24)

The Examiner further states:

Moreover, the present claims are directed to processes of using metal oxide superconductors, not processes of making them. Even if the Poole article provided direct evidence of the state of the art at the time the invention was made, which it apparently does not, that evidence still does not pertain to the issue at hand, namely, the process of using metal oxide superconductors to conduct electricity under superconducting conditions.

Applicants disagree. Poole et al. Chapter X entitled "Transport Properties" describes a process of using metal oxides superconductors to conduct electricity under superconducting conditions. Section B of Chapter X is entitled "Current Flow". A copy of Chapter X is in Attachment B of this Appeal Brief.

The Examiner further states in regard to Poole et al.:

(3) Finally, the Preface states in part at A3: "The unprecedented worldwide effort in superconductivity research that has taken place over the past two years has produced an enormous amount of experimental data on the properties of the copper oxide type materials that exhibit

superconductivity above the temperature of liquid nitrogen. ... During this period a consistent experimental description of many of the properties of the principal superconducting compounds such as BiSrCaCuO, LaSrCuO, TlBaCaCuO, and YBaCuO has emerged. ... The field of high-temperature superconductivity is still evolving ..." That preface is deemed to show that the field of high-temperature superconductivity continued to grow, on the basis of on-going basic research, after the Bednorz and Meuller article was published.

The continued growth referred to in the passage from Poole et al. quoted above does not mean that this work is not based on Applicants' initial fundamental teaching. Poole et al. as quoted above states that the unprecedented amount of work done in the short period of time after Applicants' work was because the materials "are not difficult to synthesize." Moreover, as quoted above the CCPA In re Fisher states "such an inventor should be allowed to dominate future patentable inventions of other where those inventions were based on in some way on his teachings." Moreover, the referred to future developments in the passage above are not necessarily patentably distinct from Applicants' teachings. Those who developed these compounds would have a reasonable expectation of success based on Applicants' teaching. The Examiner has provided no evidence to the contrary.

The Examiner acknowledges that the three affidavits of Dr. Tsuei, Dr. Dinger and Dr. Mitzi which were signed in May of 1998 states that the present application "includes

all known principles of ceramic fabrication known at the time the application was filed." However, the Examiner further states that the "additional indication also is considered to be a conclusory statement unsupported by particular evidence". The advisory action dated February 25, 1998 acknowledges the revised 1.132 affidavits of Mitzi, Tsuei and Dinger (filed 12/16/98) and the newly provided affidavit of Shaw (filed 12/16/98) and Dumcombe (filed 12/21/98). These revised and additional affidavits cite numerous articles and books, all published before the Applicants' filing date, which provide evidence of the general teaching of ceramic science, and in particular, ceramic fabrication techniques for transition metal oxides, more particularly for Perovskites and most particularly for the type of Perovskites of Applicants' preferred embodiments. Applicants disagree that their affidavits are conclusory. The facts are provided by Poole et al. The affidavits corroborate what Poole et al. states.

Claims 134, 135, and 137-142 were rejected under 35 U.S.C. 112, first paragraph, as based on a disclosure which is not enabling. The Examiner states "[e]ach of claims 134, 135, and 137-142 provide for a superconductor "having a  $T_c$  greater than 26°K", but those claims do not provide for a step of -- maintaining said (superconductor) at a temperature less than said  $T_c$ ". These claims have been amended by the amendment after final rejection dated June 14, 1999, to include the steps of maintaining the appropriate temperature for superconductivity as suggested by the Examiner.

In view of these arguments the Board is requested to reverse the Examiner's rejection of claims 24-26, 86-90, 96-113, 129-131, 134, 135, and 139-177 as not enabled under 35 USC 112, first paragraph.



## REJECTIONS UNDER 35 USC 112, SECOND PARAGRAPH

Claims 86-87, 96-108, 115, 118, 120, 122, 123, 129-135, and 137-142 are rejected under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

In paragraph 6-7 on page 12-16 of the final rejection, Claims 86-87, 96-108, 115, 118, 120, 122, 123, 129-135 and 137-142 have been rejected under 35 USC 112. All changes suggested by the examiner have been made by Amendment after Final Rejection dated June 14, 1999, except for those directed to the terms "layer-like", "perovskite-like", "rare-earth-like", and "layer-type". These terms occur in claims 86-87, 96-108, 112, 113, 117, 118, 122 and 123. As stated by the applicants in the prosecution these are terms of art and well understood by persons of skill in the art.

Claims 143-163 correspond to in claims 86-87, 96-108, 112, 113, 117, 118, 122 and 123. Claims 143-163 have the same wording as claims 86-87, 96-108, 112, 113, 117, 118, 122 and 123 and include all changes suggested by the examiner to overcome rejections of claims 86-87, 96-108, 112, 113, 117, 118, 122 and 123 claims under 35 USC 112, second paragraph.

The Examiner states:

a. With respect to claims 86-87 and 96-108, the terms "layer-type", "perovskite-like", "rare-earth-like" are vague and confusing.

i. The question arises: What is meant by these terms?

(1) The terms "layer-type" and "perovskite-like" are unclear because the "type" or "like" terms are deemed to be indefinite. Terms such as "like", "similar", and "type" are indefinite." It is suggested that "layer-type perovskite-like crystal structure" be changed -- a substantially layered perovskite crystal structure --.

In support of the Examiner's view of term such as "type" and "like", the Examiner cites: Ex parte Remark, 15 USPQ 2d 1498, 1500 (BPAI 1990); Ex parte Kristensen, 10 USPQ 2d 1701, 1703 (BPAI 1989); Ex parte Attig, 7 USPQ 2d 1092, 1093 (BPAI 1988); and Ex parte Copenhaver, 109 USPQ 118 (POBA 1955).

Ex parte Remark is not on point since the Board found the term "and the like" in a claim to be indefinite under §112. Applicants claims do not use this terminology.

Ex parte Kristensen is not on point since the Board found the term "similar" in the phrase "for high pressure cleaning units or similar apparatus" in a claim indefinite under §112, second paragraph. Applicants do not use the terminology "or similar". The Board held with respect to the second paragraph of §112, the inquiry is "to determine whether the claims do, in fact, set out and circumscribe a particular area with a

reasonable degree of precision and particularity". In the present application the terms "perovskite-like", "perovskite-type", "layered-like", "layered-type" and "rare-earth-like" are terms used in the art and these are well known and understood by a person of skill in the art.

Ex parte Attig is also not on point. The Board found the term "ZSM-5-type" indefinite under §112, second paragraph, because the prior art cited during prosecution gave different meanings to the term "ZSM-5-type". But the Board did not find the use of the term "type" in a claim per se indefinite. The Board says "[i]t is true that the zeolites have been defined in various patents and claimed with the terminology "ZSM-5-type". However, clearly the art of record in this case, all of it cited by applicants themselves, in the aggregate serve to render the term indefinite rather than definite". 7 USPQ 1092, 1093. The Examiner has not shown that the terms "perovskite-like", "perovskite-type", "layered-like", "layered-type" and "rare-earth-like" as used in applicants' claims have different meanings in different cited prior art. To the contrary, Applicants have shown that these terms have a uniform meaning in the transition metal oxide high  $T_c$  art.

In Ex parte Copenhaver, the Board stated in regard to the terminology "Friedel-Graftz type" catalyst.

"[w]e are of the view that the word "type" when appended to another wise definite expression so extends the scope of such an

expression as to render it objectionably indefinite from the stand point of patent law and procedures."

We are not led to a different conclusion by the fact that the expression may have been used in certain technical and scientific publications which are not subject to the rigid legal requirements for definitions that apply to patent claims. The fact that the expression may have been used in claims of certain patents likewise does not alter our view on the question."

Applicants note that Ex parte Copenhaver decided in 1955 was not cited by the Board in the later Board decisions cited by the Examiner. This decision has not been cited by any other Board or Court decision.

The Examiner states that the term "rare earth-like element" is indefinite and that the terms "type and "like" are unclear. Applicants respectfully disagree. Attachment A of Applicants' response dated November 28, 1997 is the result of a Lexis search done by the undersigned attorney. This search shows the term "rare earth like" or "rare earth and the like" used in 68 US patents. The sections of the 68 patents where these terms appears are printed using the "KWICK" function of Lexis. Attachment B of Applicants' response dated November 28, 1997 is the results of a Lexis search done by the undersigned attorney. This search shows the term "rare earth like" used in the claims of 4 issued US patents. The sections of the claims of the 4 patents where this term appears in the claims are printed using the "KWICK" function of Lexis. Consequently,

the term "rare earth like" is a term use in the art, understood by a person of skill in the art and recognized as a definite term by the USPTO for use in US patent claims.

The Examiner states that the term "perovskite-like" is indefinite. The term "perovskite-like" or "perovskite-type" is commonly used in the art. Attachment C of Applicants' response dated November 28, 1997 is the results of a Lexis search done by the undersigned attorney. This search shows that the terms "perovskite like" and "supercond!" (the "!" represents any combination of letters) are used in 107 US patents. The section of the 107 patents where these terms appears are printed using the "KWICK" function of Lexis. Attachment D of Applicants' response dated November 28, 1997 is a result of a Lexis search done by the undersigned attorney. This search shows the terms "perovskite like" or 'perovskite type" used in the claims of two issued US patents. The sections of the claims of the 2 patents where this term appears in the claims are printed using the "KWICK" function of Lexis. Attachment E of Applicants' response dated November 28, 1997 is a copy of the first page of Chapter 2 of the book "Perovskites and High Tc Superconductors" by F. S. Galasso, Gordon and Breach Scientific Publishers, 1990. Chapter 2 is entitled "Structure of Perovskite-type Compounds". Attachment F of Applicants' response dated November 28, 1997 is a copy of page 78 of the book by C. Poole, Jr. et al. Page 78 is the beginning of the section entitled "D. Perovskite-type Superconducting Structures". The first paragraph of the section states "[i]n their first report on high-temperature superconductors Bednorz and Muller (the applicants) referred to their samples as 'metallic, oxygen deficient ... perovskite like mixed valent copper compounds.' Subsequent work has confirmed that

the new superconductors do indeed have these characteristics. In this section we will comment on their perovskite-like aspects" (insert added). Consequently, the terms "perovskite like" or "perovskite type" are terms used in the art and recognized as a definite by the USPTO for use in US patent claims. (It is noted that this passage also shows that the terminology "mixed valent copper compounds" is used and understood in the art. Applicant further notes that one of the books cited in the affidavit of Peter Duncombe to demonstrate the general teaching of ceramic science includes in the title "Perovskite-Type Compounds". This book was published in 1969 showing that this term was well known and understood by those of the skill in the art long before the filing date of the present application.

The Poole et al. in Chapter VI on "Crystallographic Structures" states at page 73 "[m]uch has been said about the oxide superconductor compounds being **perovskite types**, so we will begin with a description of the perovskite structure." (emphasis added) (See Attachment I of Applicants response dated November 28, 1997).

The undersigned attorney did a search in Lexis for the terms "like" in issued US patents. As shown in Attachment A of Applicants' response dated December 27, 1997, this search Lexis found 140,058 issued US patents using the terminology "like" in the claims. The USPTO has, therefore, accepted this terminology as definite within the meaning of 35 USC 112. A number of specific examples are provided in Attachments B

of Applicants' response dated December 27, 1997, to Attachment J of Applicants' response dated December 27, 1997, each of which are the results of a similar Lexis search. (Lists of the patent numbers will be provided at the request of the Board.) Attachment B shows that there are 443 issued US patents having the term "diamond like" in the claims. Attachment C of Applicants' response dated December 27, 1997, shows that there are 319 issued US patents having the term "diamond like carbon" in the claims. Attachment D of Applicants' response dated December 27, 1997, shows that there are 10 issued US patents having the term "halogen like" in the claims. Attachment E of Applicants' response dated December 27, 1997, shows that there are 11 issued US patents having the term "oxygen like" in the claims. Attachment F of Applicants' response dated December 27, 1997, shows that there are 79 issued US patents having the term "ceramic like" in the claims. Attachment G of Applicants' response dated December 27, 1997, shows that there are 31 issued US patents having the term "carbon like" in the claims. Attachment H of Applicants' response dated December 27, 1997, shows that there are 5 issued US patents having the term "silicon like" in the claims. Attachment I of Applicants' response dated December 27, 1997, shows that there are 10 issued US patents having the term "nitrogen like" in the claims. Attachment J of Applicants' response dated December 27, 1997, shows that there are 17 issued US patents having the term "copper like" in the claims. In view thereof applicants respectfully request the Board to withdraw the rejection of their claims as indefinite for using the terminology "layer-like", "perovskite like" and "rare-earth-like" since use of the term "like" is recognized as definite under 35 USC 112 by the USPTO.

Also the term "ceramic-like" is a term commonly used in the art. Attachment M of Applicants' response dated November 28, 1997 is the result of a Lexis search performed by the undersigned attorney using the search criteria "ceramic" within one word of "like" and "copper" within one word of "oxide" and "rare" within one word of "earth". This search identified 23 issued US patents. These patents are listed in the attachment using the Lexis KWICK feature which list only those portions of the patents where these terms appear. The search was limited to this criteria since a search on "ceramic" within one word of "like" identified more than 1,000 issued US patents and a search on "ceramic" within one word of "like: in the same document as "copper" within one word of "oxide" identified more than 1000 US patents. It is clear that the term "ceramic like" is well understood in the art and is thus definite.

An affidavit under 37 CFR 1.132 of Dr. James W. Leonard, IBM research librarian was submitted on December 15, 1998. Dr. Leonard did a search of articles referencing Applicants article J. G. Bednorz and K. A. Muller, Zeitschrift fur Physik B-Condensed Matter, **64** , pp. 189-193 (Sept. 1986) which is incorporated by reference in the specification at page 6, lines 8-10. As stated at page 6 this article is the basis for applicants invention. More than 5800 articles have referenced applicants' article. This is evidence that applicants' teaching in the present application has motivated persons of skill in the art to work in the field of high  $T_c$  superconductivity and that applicants teaching has fully enabled the invention of their claims. All these articles citing applicants' article acknowledge that their work is based on Applicants' teaching.



Claims 112, 113, 117, 118, 122 and 123 have been rejected under 35 USC 112 as indefinite for using terminology "layer-type". Applicants respectfully disagree.

The undersigned attorney did a search in Lexis for the terms "layer-type" and the term "layer" preceding the term "type" by one word (layer pre/1 type). In this search Lexis found 225 issued US patents using this terminology in the claims. The USPTO has, therefore, accepted this terminology as definite within the meaning of 35 USC 112. Attachment A of the Applicants' response dated December 22, 1998, is the results of this search printed out using the .kw or "kwick" feature which prints the searched term and words before and after the searched term. The searched terminology appears in a number of forms such as "layer type", "layer-type", "layer of type". In view thereof applicants request the Board to reverse the rejection of claims 112, 113, 117, 118, 122 and 123 under 35 USC 112 as indefinite for using the terminology "layer-type".

In attachment B of the Applicants' response dated December 22, 1998, there is a search done by Jim Leonard, an IBM Research librarian, at the request of the undersigned attorney of the term "Layered like" and "layered type" in on-line non-patent literature prior to applicants' filing date. From Attachment B of the Applicants' response dated December 22, 1998, it is clear that these terms are used and understood by persons of skill in the art.

In attachment C of the Applicants' response dated December 22, 1998, there is a search done by Jim Leonard, an IBM Research librarian, at the request of the undersigned attorney of the term "rare earth like" in on-line non-patent literature prior to applicants' filing date. From this Attachment C it is clear that this term is used and understood by persons of skill in the art. This is in addition to the other evidence of the definiteness of this term to overcome the rejection of applicants claims as indefinite for using the term "rare earth like" which applicants respectfully request the Board to reverse

In Attachment D of the Applicants' response dated December 22, 1998, there is a search done by Jim Leonard, an IBM Research librarian, at the request of the undersigned attorney of the term "perovskite like" in on-line non-patent literature prior to Applicants' filing date. From this Attachment D it is clear that this term is used and understood by persons of skill in the art. This is in addition to the other evidence of the definiteness of this term to overcome the rejection of Applicants' claims as indefinite for using the term "perovskite like" which applicants respectfully request the Board to reverse.

The Examiner Further states:

- (1) The terms "layer-type" and "perovskite-like" are unclear because the "type" or "like" terms are deemed to be indefinite. Terms such as "like", "similar", and "type" are indefinite." It is suggested that "layer-type

perovskite-like crystal structure" be changed -- a substantially layered perovskite crystal structure --.

Applicants have said that person of skill in the art would understand (rare earth-like) to mean that a location occupied by a rare earth element can also be occupied by another element which would have chemical properties similar enough to the rare earth elements such that it would fit in to the lattice site occupied by the rare earth element and act chemically as a rare earth element. To this the Examiner has responded "[t]hat response does not alleviate the problem, however. Other elements may 'fit' into the lattice but they may not necessarily be 'rare-earth-like'". This comment does not address the issue. These are only about 100 elements of which 14 or 15 are rare-earth elements leaving about 86 other elements. It is not difficult for a person of skill in the art to determine which elements will behave like a rare-earth element when placed in the lattice.

Claims 112, 113, 115, 117, 118, 120, 122, and 123 have been found to be indefinite for the reasons that follow.

- i. In claim 112, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.
- ii. In claim 113, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

iv. In claim 117, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

v. In claim 118, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

viii. In claim 122, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

ix. In claim 123, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

d. Applicants' arguments filed March 7, 1997 (#59) have been fully considered but they are not persuasive.

These issues have been addressed above.

Applicants have cited numerous issued U.S. patents using "type" and "like" in the claims. Many of these patents used the identical terminology objected to by the Examiner which has been used by Applicants. Many issued U.S. patents similar terminology to that used by Applicants. The Examiner has provided no reason for rejecting Applicants claims using the terminology "layer-type", "perovskite like", "perovskite type" and "rare earth like" under §112, second paragraph as indefinite when there are issued patents using these and related terms in the claims.

In view of these arguments applicants request the Board to reverse the rejection of claims 86-87, 96-108, 115, 118, 120, 122, 123, 129-135, and 137-142 as being indefinite under 35 U.S.C. § 112, second paragraph.

1.

### **SPECIFIC ARGUMENTS AS TO EACH CLAIM**

In this section of this appeal brief the Asahi Shinbum article is referred to as ASA . The expression " the Asahi Shinbum article provides no teaching suggestion, motivation for or incentive for the limitations highlighted in the clami language above" is abbreviated as "ASA provides no TSMA for the limitation highlighted in the claim language above". In the rejection of all of applicants claims, except for claim 136, for no enablement under §112, first paragraph, the Examiner has not specifically referred to any of the rejected claims in paragraphs c to f on pages 6 to 12 which is the part of the final rejection directed to the claim rejects under §112, first paragraph. In the objection to the specification under §112, first paragraph the Examiner only refers to claims 24, 88, 96 and 103 . Applicants' comments as to dependent claims include the Applicants' comments as to the claims from which they depend even if not repeated.

The best mode contemplated at the time the present application was filed was the subject of claim 136. Support for each of the claims and how a person of skill in the art can make and use each claim is described above.

#### **Claim 24 recites:**

24. A method including the steps of forming a transition metal oxide having a phase therein which exhibits a superconducting state at a **critical temperature in excess of 26°K,**

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase, and

passing an electrical supercurrent through said transition metal oxide while it is in said superconducting state.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 25 recites:**

25. The method of claim 24, where said transition metal oxide is comprised of a transition metal capable of exhibiting **multivalent states**.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 26 recites:**

26. The method of claim 24, where said transition metal oxide is comprised of a Cu oxide.

See comments for claim 24.

**Claim 86 recites:**

86. A method, comprising the steps of:

forming a composition including a transition metal, **a rare earth or rare earth-like element, an alkaline earth element, and oxygen, where said composition is a mixed transition metal oxide having a non-stoichiometric amount of oxygen therein** and exhibiting a superconducting state at a temperature greater than 26°K,

maintaining said composition in said superconducting state at a **temperature greater than 26°K, and**

passing an electrical current through said composition while said composition is in said superconducting state.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot



practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art. As to "like" or " type" terminology being indefinite under §112, second paragraph see the discussion above.

**Claim 87 recites:**

87. The method of claim 86, where said transition metal is copper.

See the discussion for claim 86.

**Claim 88 recites**

88. A method, including the steps of:

forming a composition exhibiting a superconductive state at a temperature  
**in excess of 26°K**, maintaining said composition at a temperature in  
excess of 26°K at which temperature said composition exhibits said  
superconductive state, and

passing an electrical current through said composition while said  
composition is in said superconductive state.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph

the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 89 recites:**

89. The method of claim 88, where said composition is comprised of a metal oxide.

See the comments for claim 88.

**Claim 90 recites:**

90. The metal of claim 88, where said composition is comprised of a transition metal oxide.

See the comments for claim 88.

**Claim 96 recites:**

96. A superconductive method for causing electric current flow in a superconductive state at a temperature in excess of 26 K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **layer-type** perovskite-like crystal

structure, the composition having a superconductor **transition temperature  $T_c$  of greater than 26 K**;

(b) maintaining the superconductor element at a temperature above 26 K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art. As to “like” or “ type” terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 97 recites:**

97. The superconductive method according to claim 96 in which the copper-oxide compound of the superconductive composition **includes at least one rare-earth or rare-earth-like element and at least one alkaline-earth element.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art. As to "like" or " type" terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 98 recites:**

98. The superconductive method according to claim 97 in which the rare-earth or rare-earth-like element is lanthanum.

See comments for claim 97.

**Claim 99 recites:**

99. The superconductive method according to claim 97 in which the alkaline-earth element is barium.

See comments for claim 97.

**Claim 100 recites:**

100. The superconductive method according to claim 96 in which the copper-oxide compound of the superconductive composition includes **mixed valent copper ions.**

In addition to the comments on claim 96, as the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 101 recites:**

101. The superconductive method according to claim 100 in which the  
**copper-oxide compound includes at least one element in a  
nonstoichiometric atomic proportion.**

In addition to the comments on claim 100. As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 102 recites:**

102. The superconductive method according to claim 101 in which  
**oxygen is present** in the copper-oxide compound **in a  
nonstoichiometric atomic proportion.**

In addition to the comments on claim 101, as the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 103 recites:**

103. A superconductive method for conducting an electric current  
essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **layer-type** perovskite-like crystal structure, the copper-oxide compound **including at least one rare-earth or rare-earth-like element and at least one alkaline-earth element**, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26 K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art. As to "like" or "type" terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 104 recites:**

104. The superconductive method according to claim 103 in which the rare-earth or rare-earth-like element is lanthanum.

See comments on claim 103.

**Claim 105 recites:**

105. The superconductive method according to claim 103 in which the alkaline-earth element is barium.

See comments on claim 103.

**Claim 106 recites:**

106. The superconductive method according to claim 103 in which the copper-oxide compound of the superconductive composition includes **mixed valent copper ions**.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art. As to “like” or “ type” terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 107 recites:**

107. The superconductive method according to claim 106 in which the copper-oxide compound includes at least one element in a **nonstoichiometric atomic proportion.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art. As to "like" or " type" terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 108 recites:**

108. The superconductive method according to claim 107 in which oxygen is present in the copper-oxide compound in a **nonstoichiometric atomic proportion.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a



person of skill in the art. As to "like" or "type" terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 108 recites:**

109. A method including the steps of forming copper oxide having a phase therein which exhibits a superconducting state at **a critical temperature in excess of 26°K;**

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said superconducting state;

said copper oxide includes **at least one element selected from the group consisting of a Group II A element, a rare earth element and a Group III B element.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot

practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 110 recites:**

110. A method comprising the steps of:

forming a composition including copper, oxygen and an element selected from the group consisting of a Group II A element, a rare earth element and a Group III B element, where **said composition is a mixed copper oxide having a non-stoichiometric amount of oxygen therein** and exhibiting a superconducting state **at a temperature greater than 26°K;**

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 111 recites:**

111. A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature  
**in excess of 26°K;**

maintaining said composition at a temperature in excess of 26°K at which  
temperature said composition exhibits said superconductive state;

passing an electrical current through said composition while said  
composition is in said superconductive state; and

said composition including a copper oxide and an element selected from  
the group consisting of Group II A element, a rare earth element and a  
Group III B element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 112 recites:**

112. A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

- (a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **layer-type** perovskite-like crystal structure, the composition having a superconductive transition temperature  **$T_c$  of greater than 26°K**, said superconductive composition includes **at least one element selected from the group consisting of a Group II A element, a rare earth element; and a Group III B element;**
- (b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and
- (c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art. As to “like” or “type” terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 113 recites:**

113. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

- (a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **layer-type** perovskite-like crystal structure, the copper-oxide compound including **at least one element selected from the group consisting of a Group II A element, a rare earth element and a Group III B element**, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;
- (b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and
- (c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art. As to “like” or “ type” terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 114 recites:**

114. A method including the steps of forming copper oxide having a phase therein which exhibits a superconducting state at a critical temperature **in excess of 26°K;**

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said superconducting state;

**said copper oxide includes at least one element selected from the group consisting of a Group II A element and at least one element**

**selected from the group consisting of a rare earth element and a Group III B element.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 115 recites:**

115. A method comprising the steps of:

**forming a composition including copper, oxygen and an element selected from the group consisting of at least one Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, where said composition is a mixed copper oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K;**

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 116 recites:**

116. A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature  
**in excess of 26°K;**

maintaining said composition at a temperature in excess of 26°K at which  
temperature said composition exhibits said superconductive state;

passing an electrical current through said composition while said  
composition is in said superconductive state; and

**said composition including a copper oxide and at least one element  
selected from the group consisting of Group II A and at least one  
element selected from the group consisting of a rare earth element  
and a Group III B element.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.



**Claim 117 recites:**

117. A superconductive method for causing electric-current flow in a superconductive state at a temperature **in excess of 26°K**, comprising:

- (a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having **a layer-type** perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition **includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;**
- (b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and
- (c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 118 recites:**

118. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

- (a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **layer-type** perovskite-like crystal structure, the copper-oxide compound **including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element**, the composition having a superconductive/resistive transition defining a superconductive-resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;
- (b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and
- (c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to “like” or “ type” terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 119 recites:**

119. A method including the steps of forming a transition metal oxide having a phase therein which exhibits a superconducting state at a critical temperature **in excess of 26°K;**

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said superconducting state;

**said transitional metal oxide includes at least one element selected from the group consisting of a Group II A element and at lest one element selected from the group consisting of a rare earth element and a Group III B element.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 120 recites:**

120. A method comprising the steps of:

forming a composition including a transition metal, **oxygen and an element selected from the group consisting of at least one Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element**, where said composition is a mixed transitional metal oxide formed from said transition metal and said oxygen, said mixed transition metal oxide having a **non-stoichiometric amount of oxygen** therein and exhibiting a superconducting state at a **temperature greater than 26°K;**

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to “like” or “type” terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 121 recites:**

121. A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature  
**in excess of 26°K;**

maintaining said composition at a temperature in excess of 26°K at which  
temperature said composition exhibits said superconductive state;

passing an electrical current through said composition while said  
composition is in said superconductive state; and

**said composition including a transitional metal oxide and at least  
one element selected from the group consisting of Group II A  
element and at least one element selected from the group consisting  
of a rare earth element and a Group III B element.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Calim 122 recites:**

122. A superconductive method for causing electric-current flow in a superconductive state at a temperature **in excess of 26°K**, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal oxide compound having a **layer-type** perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes **at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;**

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to “like” or “type” terminology being indefinite under §112, second paragraph, see the discussion above.

**Calim 123 recites:**

123. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal-oxide compound having a **layer-type** perovskite-like crystal structure, the transition metal-oxide compound including **at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element**, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  **being greater than 26°K;**

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to “like” or “type” terminology being indefinite under §112, second paragraph, see the discussion above.

**Calim 124 recites:**

124. A method including the steps of forming copper oxide having a phase therein which exhibits a superconducting state at a critical temperature **in excess of 26°K**;

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said superconducting state;



said copper oxide includes at least **one element selected from group consisting of a Group II A element, at least one element selected from the group consisting of a rare earth element and at least one element selected from the group consisting of a Group III B element.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 125 recites:**

125. A method comprising the steps of:

forming a composition including **copper, oxygen and an element selected from the group consisting of at least one Group II A element and at least one element selected from the group consisting of a rare earth element at least one element selected from the group consisting of a Group III B element, where said composition is a mixed copper oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K;**

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 126 recites:**

126. A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature **in excess of 26°K;**

maintaining said composition at a temperature in excess of 26°K at which temperature said composition exhibits said superconductive state;

passing an electrical current through said composition while said composition is in said superconductive state; and

said composition including a copper oxide **and at least one element selected from the group consisting of Group II A element, at least one element selected from the group consisting of a rare earth**

element and at least one element selected from the group consisting of a Group III B element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 127 recites:**

127. A superconductive method for causing electric-current flow in a superconductive state at a temperature **in excess of 26°K, comprising:**

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting

essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition **includes at least one element selected from the group consisting of a Group II A element, at least one element selected from the group consisting of a rare earth element and at least one element selected from the group consisting of a Group III B element;**

(b) maintaining the superconductor element at a temperature above 26°K  
and below the superconductor transition temperature  $T_c$  of the  
superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation  
highlighted in the claim language above.

**Claim 128 recites:**

128. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

- (a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **layer-type** perovskite-like crystal structure, the copper-oxide compound including **at least one element selected from the group consisting of a group II A element, at least one element selected from the group consisting of a rare earth element and at least one element selected from the group consisting of a Group III B element**, the composition having a superconductive-resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;
- (b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above.

**Claim 129 recites:**

129. A method comprising providing a composition having a transition temperature **greater than** 26°K, the composition including a rare earth or alkaline earth element, a transition metal element capable of exhibiting **multivalent states** and oxygen, including at least one phase that exhibits superconductivity at temperature in excess of 26°K, maintaining said composition at said temperature to exhibit said superconductivity and passing an electrical superconducting current through said composition with said phrase exhibiting said superconductivity.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 130 recites:**

130. A method comprising providing a superconducting transition metal oxide having a superconductive onset temperature **greater than 26°K**, maintaining said superconducting transition metal oxide at a temperature less than said superconducting onset temperature and flowing a superconducting current therein.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 131 recites:**

131. A method comprising providing a superconducting copper oxide having a superconductive onset temperature **greater than 26°K**, maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a superconducting current in said superconducting oxide.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 132 recites:**

132. A method comprising providing a superconducting oxide composition having a superconductive onset temperature **greater than 26°K**, maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a superconducting current therein, said composition comprising at least one each of rare earth, an alkaline earth, and copper.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 133 recites:**



133. A method comprising providing a superconducting oxide composition having a superconductive onset **temperature greater than 26°K**, maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a superconducting electrical current therein, said composition comprising at least one each of a Group III B element, an alkaline earth, and copper.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 134 recites:**

134. A method comprising flowing a superconducting electrical current in a transition metal oxide having a  $T_c$  **greater than 26°K** and maintaining said transition metal oxide at a temperature less than said  $T_c$ .

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Calim 135 recites:**

135. A method comprising flowing a superconducting current in a copper oxide having a  $T_c$  **greater than 26°K** and maintaining said copper oxide at a temperature less than said  $T_c$ .

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 136 is allowed.**

**Claim 137 recites:**

137. A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  **greater than 26°K**, said composition comprising at least one each of a III B element, an alkaline earth, and copper oxide and maintaining said composition of matter at a temperature less than  $T_c$ .

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 138 recites:**

138. A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  **greater than 26°K**, said composition comprising at least one each of a rare earth, alkaline earth, and copper oxide and maintaining said composition of matter at a temperature less than said  $T_c$ .

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 139 recites:**

139. A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  **greater than 26°K**, said composition

comprising at least one each of a rare earth, and copper oxide and  
maintaining said composition of matter at a temperature less than said  $T_c$ .

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 140 recites:**

140. A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  **greater than 26°K** carrying, said composition comprising at least one each of a III B element, and copper oxide and maintaining said composition of matter at a temperature less than said  $T_c$ .

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 141 recites:**

141. A method comprising flowing a superconducting electrical current in a transition metal oxide comprising a  $T_c > 26^\circ\text{K}$  and maintaining said transition metal oxide at a temperature less than said  $T_c$ .

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 142 recites:**

142. A method comprising flowing a superconducting electrical current in a copper oxide composition of matter comprising a  $T_c > 26^\circ\text{K}$  and maintaining said copper oxide composition of matter at a temperature less than said  $T_c$ .

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 143 recites:**

143. A method, comprising the steps of:

forming a composition including a transition metal, a group IIIB element, an alkaline earth element, and oxygen, where said composition is a **mixed transition metal oxide having a non-stoichiometric amount of oxygen** therein and exhibiting a superconducting state at a temperature **greater than 26°K,**

maintaining said composition in said superconducting state at a temperature greater than 26°K, and

passing an electrical current through said composition while said composition is in said superconducting state.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 144 recites:**

144. The method of claim 143, where said transition metal is copper.

See comments for claim 143.

**Claim 154 recites:**

145. A superconductive method for causing electric current flow in a superconductive state at a temperature **in excess of 26 K**, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **substantially layered** perovskite crystal structure, the composition having a superconductor transition temperature  $T_c$  of greater than 26 K;

b) maintaining the superconductor element at a temperature above 26 K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 146 recites:**

146. The superconductive method according to claim 145 in which the copper-oxide compound of the superconductive composition includes **at least one element selected from the group consisting of a rare-earth element and a Group III B element and at least one alkaline-earth element.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 147 recites:**

147. The superconductive method according to claim 146 in which the rare-earth or rare-earth-like element is lanthanum.

See the comments as to claim 146 and as to "like" or "type" terminology being indefinite under §112, second paragraph, see the discussion above.

**Claim 148 recites:**

148. The superconductive method according to claim 146 in which the alkaline-earth element is barium.

See commnets as to claim 46.



**Claim 149 recites:**

149. The superconductive method according to claim 145 in which the copper-oxide compound of the superconductive composition includes **mixed valent copper ions.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 150 recites:**

150. The superconductive method according to claim 149 in which the copper-oxide compound includes at least one element in a **nonstoichiometric atomic proportion.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 151 recites:**

151. The superconductive method according to claim 150 in which oxygen is present in the copper-oxide compound in a **nonstoichiometric atomic proportion**.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claims 152 recites:**

152. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **substantially layered** perovskite crystal structure, the copper-oxide compound **including at least one element selected from the group consisting of a rare-earth element and a Group III B element and at least one alkaline-earth element**, the composition having a superconductive/resistive transition defining a

superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$ , the transition-onset temperature  $T_c$  **being greater than 26 K**;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 153 recites:**

153. The superconductive method according to claim 152 in which said at least one element is lanthanum.

See comments as to claim 152.

**Claim 154 recites:**

154. The superconductive method according to claim 152 in which the alkaline-earth element is barium.

See comments as to claim 152.

**Claim 155 recites:**

155. The superconductive method according to claim 152 in which the copper-oxide compound of the superconductive composition **includes mixed valent copper ions.**

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 156 recites:**

156. The superconductive method according to claim 155 in which the copper-oxide compound includes at least one element in a **nonstoichiometric atomic proportion.**

In addition to comments on claim 155 , as the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 157 recites:**

157. The superconductive method according to claim 156 in which oxygen is present in the copper-oxide compound in a **nonstoichiometric atomic proportion**.

In addition to comments on claim 156, as the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 158 recites:**

158. A superconductive method for causing electric-current flow in a superconductive state at a temperature **in excess of 26°K**, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a

copper-oxide compound having a **substantially layered** perovskite crystal structure, the composition having a superconductive transition temperature  **$T_c$  of greater than 26°K**, said superconductive composition includes **at least one element selected from the group consisting of a Group II A element, a rare earth element; and a Group III B element;**

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 159 recites:**

159. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **substantially layered** perovskite crystal structure, the copper-oxide compound including **at least one element selected from the group consisting of a Group II A element, a rare earth element and a Group III B element**, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  **$T_c$  being greater than 26°K**;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claims 160 recites:**

160. A superconductive method for causing electric-current flow in a superconductive state at a temperature **in excess of 26°K**, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **substantially layered** perovskite crystal structure, the composition having a superconductive transition temperature **T<sub>c</sub> of greater than 26°K**, said superconductive composition includes **at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element**;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature T<sub>c</sub> of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot



practice the invention of this claim from applicants teaching and from what is known to a person of skill in the art.

**Claim 161 recites:**

161. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a **substantially layered** perovskite crystal structure, the copper-oxide **compound including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element**, the composition having a superconductive/resistive transition defining a superconductive-resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  **being greater than 26°K**;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 162 recites:**

162. A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal oxide compound having a substantially layered perovskite crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group **consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;**

(b) maintaining the superconductor element at a temperature **above 26°K** and below the superconductor transition  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 163 recites:**

163. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal-oxide compound having a **substantially layered** perovskite crystal structure, the transition metal-oxide compound including **at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element**, the

composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 164 recites:**

164. A method according to claim 129 wherein said composition comprises a **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 165 recites:**

165. A method according to claim 130 wherein said superconducting transistor metal oxide comprises a **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 166 recites:**

166. A method according to claim 131 wherein said superconducting copper oxide comprises a **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 167 recites:**

167. A method according to claim 132 wherein said superconducting oxide composition comprises a substantially layered perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 168 recites:**

168. A method according to claim 133 wherein said superconducting oxide composition comprises a substantially **layered perovskite** crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 169 recites:**

169. A method according to claim 134 wherein said transistor metal oxide comprises a **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 170 recites:**

170. A method according to claim 135 wherein said copper oxide comprises a **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph

the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 171 recites:**

171. A method according to claim 136 wherein said composition comprises a **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 172 recites:**

172. A method according to claim 137 wherein said composition of matter comprises a **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.



**Claim 173 recites:**

173. A method according to claim 138 wherein said composition of matter comprises **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 174 recites:**

174. A method according to claim 139 wherein said composition of matter comprises a **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 175 recites:**

175. A method according to claim 140 wherein said composition of matter comprises **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 176 recites**

176. A method according to claim 141 wherein said transistor metal oxide comprises **substantially layered** perovskite crystal structure.

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

**Claim 177 recites:**

177. A method according to claim 142 wherein said copper oxide composition comprises **substantially layered** perovskite crystal structure

As the rejections under §102(a) and §103(a) ASA provides no TSMA for the limitation highlighted in the claim language above. As to enablement under §112, first paragraph the Examiner has provided no extrinsic evidence that a person of skill in the art cannot practice the invention of this claim from applicants teaching and from what is know to a person of skill in the art.

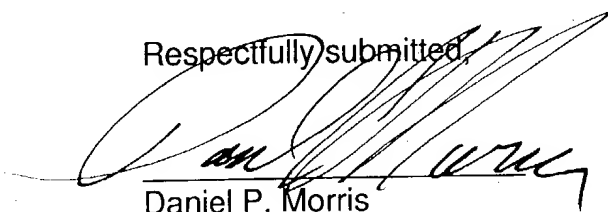
## CONCLUSION

In view of the argument herein, Applicants request the Board:

1. reverse the determination that claims 24-26, 86-90, 96-135 and 137-177 are not supported by the priority document;
2. reverse the rejection of claims 24-26, 86-90, 96-135 and 137-177 as anticipated under 35 USC 102(a) by the Asahi Shinbum article;
3. reverse the rejection of claims 24-26, 86-90, 96-135 and 137-177 as obvious under 35 USC 103(a) in view of the Asahi Shinbum article;
4. reverse the rejection of claims 24-26, 86-90, 96-135 and 137-142 as not enabled under 35 USC 112, first paragraph; and
5. reverse the rejection of claims 86-87, 96-108, 115, 118, 120, 122, 123, 124, 129-135 and 137-142 indefinite under 35 USC 112 second paragraph.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

Respectfully submitted,



Daniel P. Morris  
Reg. No. 32,053  
(914) 945-3217

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218

## APPENDIX

### CLAIMS

24. A method including the steps of forming a transition metal oxide having a phase therein which exhibits a superconducting state at a critical temperature in excess of 26°K,

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase, and

passing an electrical supercurrent through said transition metal oxide while it is in said superconducting state.

25. The method of claim 24, where said transition metal oxide is comprised of a transition metal capable of exhibiting multivalent states.

26. The method of claim 24, where said transition metal oxide is comprised of a Cu oxide.

86. A method, comprising the steps of:

forming a composition including a transition metal, a rare earth or rare earth-like element, an alkaline earth element, and oxygen, where said composition is a mixed

transition metal oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K,

maintaining said composition in said superconducting state at a temperature greater than 26°K, and

passing an electrical current through said composition while said composition is in said superconducting state.

87. The method of claim 86, where said transition metal is copper.

88. A method, including the steps of:

forming a composition exhibiting a superconductive state at a temperature in excess of 26°K, maintaining said composition at a temperature in excess of 26°K at which temperature said composition exhibits said superconductive state, and

passing an electrical current through said composition while said composition is in said superconductive state.

89. The method of claim 88, where said composition is comprised of a metal oxide.

90. The metal of claim 88, where said composition is comprised of a transition metal oxide.

96. A superconductive method for causing electric current flow in a superconductive state at a temperature in excess of 26 K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the composition having a superconductor transition temperature  $T_c$  of greater than 26 K;

(b) maintaining the superconductor element at a temperature above 26 K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

97. The superconductive method according to claim 96 in which the copper-oxide compound of the superconductive composition includes at least one rare-earth or rare-earth-like element and at least one alkaline-earth element.

98. The superconductive method according to claim 97 in which the rare-earth or rare-earth-like element is lanthanum.

99. The superconductive method according to claim 97 in which the alkaline-earth element is barium.

100. The superconductive method according to claim 96 in which the copper-oxide compound of the superconductive composition includes mixed valent copper ions.

101. The superconductive method according to claim 100 in which the copper-oxide compound includes at least one element in a nonstoichiometric atomic proportion.

102. The superconductive method according to claim 101 in which oxygen is present in the copper-oxide compound in a nonstoichiometric atomic proportion.

103. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the copper-oxide compound including at least one rare-earth or rare-earth-like element and at least one alkaline-earth element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$ , the transition-onset temperature  $T_c$  being greater than 26 K;



(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

104. The superconductive method according to claim 103 in which the rare-earth or rare-earth-like element is lanthanum.

105. The superconductive method according to claim 103 in which the alkaline-earth element is barium.

106. The superconductive method according to claim 103 in which the copper-oxide compound of the superconductive composition includes mixed valent copper ions.

107. The superconductive method according to claim 106 in which the copper-oxide compound includes at least one element in a nonstoichiometric atomic proportion.

108. The superconductive method according to claim 107 in which oxygen is present in the copper-oxide compound in a nonstoichiometric atomic proportion.

109. A method including the steps of forming copper oxide having a phase therein which exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said superconducting state;

said copper oxide includes at least one element selected from the group consisting of a Group II A element, a rare earth element and a Group III B element.

110. A method comprising the steps of:

forming a composition including copper, oxygen and an element selected from the group consisting of a Group II A element, a rare earth element and a Group III B element, where said composition is a mixed copper oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K;

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

111. A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature in excess of 26°K;

maintaining said composition at a temperature in excess of 26°K at which temperature said composition exhibits said superconductive state;

passing an electrical current through said composition while said composition is in said superconductive state; and

said composition including a copper oxide and an element selected from the group consisting of Group II A element, a rare earth element and a Group III B element.

112. A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition

includes at least one element selected from the group consisting of a Group II A element, a rare earth element; and a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

113. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a Group II A element, a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

114. A method including the steps of forming copper oxide having a phase therein which exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said superconducting state;

said copper oxide includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element.

115. A method comprising the steps of:

forming a composition including copper, oxygen and an element selected from the group consisting of at least one Group II A element and at least one element selected

from the group consisting of a rare earth element and a Group III B element, where said composition is a mixed copper oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K;

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

116. A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature in excess of 26°K;

maintaining said composition at a temperature in excess of 26°K at which temperature said composition exhibits said superconductive state;

passing an electrical current through said composition while said composition is in said superconductive state; and

said composition including a copper oxide and at least one element selected from the group consisting of Group II A and at least one element selected from the group consisting of a rare earth element and a Group III B element.

117. A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

118. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive-resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

119. A method including the steps of forming a transition metal oxide having a phase therein which exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;



passing an electrical supercurrent through said copper oxide while it is in said superconducting state;

said transitional metal oxide includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element.

120. A method comprising the steps of:

forming a composition including a transition metal, oxygen and an element selected from the group consisting of at least one Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, where said composition is a mixed transitional metal oxide formed from said transition metal and said oxygen, said mixed transition metal oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K;

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

121. A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature in excess of 26°K;

maintaining said composition at a temperature in excess of 26°K at which temperature said composition exhibits said superconductive state;

passing an electrical current through said composition while said composition is in said superconductive state; and

said composition including a transitional metal oxide and at least one element selected from the group consisting of Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element.

122. A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal oxide compound having a layer-type perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive

composition includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

123. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal-oxide compound having a layer-type perovskite-like crystal structure, the transition metal-oxide compound including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

124. A method including the steps of forming copper oxide having a phase therein which exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said superconducting state;

said copper oxide includes at least one element selected from group consisting of a Group II A element, at least one element selected from the group consisting of a rare earth element and at least one element selected from the group consisting of a Group III B element.

125. A method comprising the steps of:

forming a composition including copper, oxygen and an element selected from the group consisting of at least one Group II A element and at least one element selected from the group consisting of a rare earth element at least one element selected from the group consisting of a Group III B element, where said composition is a mixed copper oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K;

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

126. A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature in excess of 26°K;

maintaining said composition at a temperature in excess of 26°K at which temperature said composition exhibits said superconductive state;

passing an electrical current through said composition while said composition is in said superconductive state; and

said composition including a copper oxide and at least one element selected from the group consisting of Group II A element, at least one element selected from the group consisting of a rare earth element and at least one element selected from the group consisting of a Group III B element.

127. A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting

essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element, at least one element selected from the group consisting of a rare earth element and at least one element selected from the group consisting of a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

128. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a group II A element, at least one element selected from the group consisting of a rare earth element and at least one element selected from the group consisting of a Group III B element, the composition having a superconductive-resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

129. A method comprising providing a composition having a transition temperature greater than 26°K, the composition including a rare earth or alkaline earth element, a transition metal element capable of exhibiting multivalent states and oxygen, including at least one phase that exhibits superconductivity at temperature in excess of 26°K, maintaining said composition at said temperature to exhibit said superconductivity and passing an electrical superconducting current through said composition with said phase exhibiting said superconductivity.

130. A method comprising providing a superconducting transition metal oxide having a superconductive onset temperature greater than 26°K, maintaining said superconducting transition metal oxide at a temperature less than said superconducting onset temperature and flowing a superconducting current therein.

131. A method comprising providing a superconducting copper oxide having a superconductive onset temperature greater than 26°K, maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a superconducting current in said superconducting oxide.

132. A method comprising providing a superconducting oxide composition having a superconductive onset temperature greater than 26°K, maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a superconducting current therein, said composition comprising at least one each of rare earth, an alkaline earth,



and copper.

133. A method comprising providing a superconducting oxide composition having a superconductive onset temperature greater than 26°K, maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a superconducting electrical current therein, said composition comprising at least one each of a Group III B element, an alkaline earth, and copper.

134. A method comprising flowing a superconducting electrical current in a transition metal oxide having a  $T_c$  greater than 26°K and maintaining said transition metal oxide at a temperature less than said  $T_c$ .

135. A method comprising flowing a superconducting current in a copper oxide having a  $T_c$  greater than 26°K and maintaining said copper oxide at a temperature less than said  $T_c$ .

136. A method comprising the steps of:

forming a composition of the formula  $Ba_xLa_{x-5}, Cu_5O_y$ , wherein x is from about 0.75 to about 1 and y is the oxygen deficiency resulting from annealing said composition at temperatures from about 540°C to about 950°C and for times of about 15 minutes to about 12 hours, said composition having a metal oxide phase which exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said composition at a temperature less than said critical temperature to induce said superconducting state in said metal oxide phase; and

passing an electrical current through said composition while said metal oxide phase is in said superconducting state.

137. A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  greater than 26°K, said composition comprising at least one each of a III B element, an alkaline earth, and copper oxide and maintaining said composition of matter at a temperature less than  $T_c$ .

138. A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  greater than 26°K, said composition comprising at least one each of a rare earth, alkaline earth, and copper oxide and maintaining said composition of matter at a temperature less than said  $T_c$ .

139. A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  greater than 26°K, said composition comprising at least one each of a rare earth, and copper oxide and maintaining said composition of matter at a temperature less than said  $T_c$ .

140. A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  greater than 26°K carrying, said composition comprising at least

one each of a III B element, and copper oxide and maintaining said composition of matter at a temperature less than said  $T_c$ .

141. A method comprising flowing a superconducting electrical current in a transition metal oxide comprising a  $T_c > 26^\circ\text{K}$  and maintaining said transition metal oxide at a temperature less than said  $T_c$ .

142. A method comprising flowing a superconducting electrical current in a copper oxide composition of matter comprising a  $T_c > 26^\circ\text{K}$  and maintaining said copper oxide composition of matter at a temperature less than said  $T_c$ .

143. A method, comprising the steps of:

forming a composition including a transition metal, a group IIIB element, an alkaline earth element, and oxygen, where said composition is a mixed transition metal oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than  $26^\circ\text{K}$ ,

maintaining said composition in said superconducting state at a temperature greater than  $26^\circ\text{K}$ , and

passing an electrical current through said composition while said composition is in said superconducting state.

144. The method of claim 143, where said transition metal is copper.

145. A superconductive method for causing electric current flow in a superconductive state at a temperature in excess of 26 K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the composition having a superconductor transition temperature  $T_c$  of greater than 26 K;

b) maintaining the superconductor element at a temperature above 26 K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

146. The superconductive method according to claim 145 in which the copper-oxide compound of the superconductive composition includes at least one element selected from the group consisting of a rare-earth element and a Group III B element and at least one alkaline-earth element.

147. The superconductive method according to claim 146 in which the rare-earth or rare-earth-like element is lanthanum.

148. The superconductive method according to claim 146 in which the alkaline-earth element is barium.

149. The superconductive method according to claim 145 in which the copper-oxide compound of the superconductive composition includes mixed valent copper ions.

150. The superconductive method according to claim 149 in which the copper-oxide compound includes at least one element in a nonstoichiometric atomic proportion.

151. The superconductive method according to claim 150 in which oxygen is present in the copper-oxide compound in a nonstoichiometric atomic proportion.

152. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a rare-earth element and a Group III B element and at least one alkaline-earth element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an

effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26 K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

153. The superconductive method according to claim 152 in which said at least one element is lanthanum.

154. The superconductive method according to claim 152 in which the alkaline-earth element is barium.

155. The superconductive method according to claim 152 in which the copper-oxide compound of the superconductive composition includes mixed valent copper ions.

156. The superconductive method according to claim 155 in which the copper-oxide compound includes at least one element in a nonstoichiometric atomic proportion.

157. The superconductive method according to claim 156 in which oxygen is present in the copper-oxide compound in a nonstoichiometric atomic proportion.

158. A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

- (a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element, a rare earth element; and a Group III B element;
- (b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and
- (c) causing an electric current to flow in the superconductor element.

159. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

- (a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a Group II A

element, a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

160. A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;



(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

161. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive-resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

162. A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal oxide compound having a substantially layered perovskite crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

163. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal-oxide

compound having a substantially layered perovskite crystal structure, the transition metal-oxide compound including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

164. A method according to claim 129 wherein said composition comprises a substantially layered perovskite crystal structure.

165. A method according to claim 130 wherein said superconducting transistor metal oxide comprises a substantially layered perovskite crystal structure.

166. A method according to claim 131 wherein said superconducting copper oxide comprises a substantially layered perovskite crystal structure.

167. A method according to claim 132 wherein said superconducting oxide composition comprises a substantially layered perovskite crystal structure.

168. A method according to claim 133 wherein said superconducting oxide composition comprises a substantially layered perovskite crystal structure.

169. A method according to claim 134 wherein said transistor metal oxide comprises a substantially layered perovskite crystal structure.

170. A method according to claim 135 wherein said copper oxide comprises a substantially layered perovskite crystal structure.

171. A method according to claim 136 wherein said composition comprises a substantially layered perovskite crystal structure.

172. A method according to claim 137 wherein said composition of matter comprises a substantially layered perovskite crystal structure.

173. A method according to claim 138 wherein said composition of matter comprises a substantially layered perovskite crystal structure.

174. A method according to claim 139 wherein said composition of matter comprises a substantially layered perovskite crystal structure.

175. A method according to claim 140 wherein said composition of matter comprises substantially layered perovskite crystal structure.

176. A method according to claim 141 wherein said transistor metal oxide comprises substantially layered perovskite crystal structure.

177. A method according to claim 142 wherein said copper oxide composition comprises substantially layered perovskite crystal structure.

**ATTACHMENT A**

# *Inorganic Chemistry*

AN ADVANCED TEXTBOOK

THERALD MOELLER

Associate Professor of Chemistry  
University of Illinois

*New York · JOHN WILEY & SONS, Inc.*

*London · CHAPMAN & HALL, Limited*

*Attachment A pages*

COPYRIGHT, 1952

BY  
JOHN WILEY & SONS, INC.

*All Rights Reserved*

*This book or any part thereof must not be reproduced in any form without the written permission of the publisher.*

Library of Congress Catalog Card Number: 52-7487

PRINTED IN THE UNITED STATES OF AMERICA

Attachment A page 2

Emphasis upon quite generally inorganic chemistry, inorganic chemistry, and, sub- strongly emphasized. More recently, inorganic chemistry rather than upon remarkable the and continue to position that it

Unfortunately expanded in a university student their freshman courses. These students with the them of its scope that is to be done they have concentrated technology. Sober reflection modern and ac

For a number semester lecture the field from existing problems advanced and. At the graduate upon which the chemistry are enrollments are

Those who have suitable textbooks sequence, they



[illegible]

rate compounds  
of importance

component. This crystal together, of suitable size,

may result from  
of the crystal or

t the time when

interest but are possible arrangements lead to them is

DS

rets of chemistry.  
pon bond forma-  
, and its applica-  
chemical combina-  
t departure from  
to not possess the  
ic considerations  
non-stoichiomet-  
(1950); *Research*, 1,

ric compounds as opposed to the normal Daltonide or stoichiometric compounds. As examples, one may cite certain metallic hydrides such as  $\text{VH}_{0.56}$ ,  $\text{CeH}_{2.69}$  (p. 411); certain oxides such as  $\text{TiO}_{1.7-1.8}$ ,  $\text{FeO}_{1.056}$ ,  $\text{WO}_{2.88-2.92}$ ; such sulfides, selenides, and tellurides as  $\text{Cu}_{1.7}\text{S}$ ,  $\text{Cu}_{1.6}\text{Se}$ ,  $\text{Cu}_{1.66}\text{Te}$ ,  $\text{CuFeS}_{1.94}$ ; the tungsten bronzes,  $\text{Na}_x\text{WO}_3$ ; etc. Combinations of these types are particularly common among minerals.

Lack of true stoichiometry of this type is associated with so-called *defect crystal lattices*. Defects in a crystal lattice amount to variations from the regularity which characterizes the material as a whole. They are of two types:

1. *Frenkel defects*, in which certain atoms or ions have migrated to interstitial positions some distance removed from the "holes" which they vacated.

2. *Schottky defects*, in which "holes" are left in random fashion throughout the crystal because of migration of atoms or ions to the surface of the material.

Although both types of defect probably characterize crystals of non-stoichiometric compounds, the Schottky defects are the more important. Obviously detectable departure from true stoichiometric composition can result only if serious defects are present. It would follow, therefore, that many apparently stoichiometric compounds are not truly so. If excess metal is present in a crystal, it may also result from partial reduction of high-valent cations; whereas if excess non-metal is present, higher valent cations or lower valent anions than those normally present may be responsible. Many instances are known of multiple oxidation number in a single crystal. Non-stoichiometric compounds often show semi-conductivity, fluorescence, and centers of color. For a comprehensive discussion of this rather complex subject, a detailed review<sup>90</sup> should be consulted.

## SUMMARY OF BOND TYPES

The important linkages which hold together the components of crystalline solids and their general characteristics may be summarized as follows:

1. *Ionic linkages*, in which the crystals are made up of regular geometrical arrangements of positive and negative ions. Such solids tend to possess high melting and boiling points, are hard and difficult to deform, and tend to be soluble in polar solvents. When dissolved in such solvents or fused, they are excellent conductors. Crystals

<sup>90</sup> J. S. Anderson: *Ann. Reports*, **43**, 104 (1946).

Attachment A page 3

overcome. Such cage compounds have been called *clathrate* compounds<sup>89</sup> (Latin *clathratus*, enclosed by cross bars of a grating). In general, they occur when mixtures of the components are crystallized under optimum conditions. Their properties are roughly those of the enclosing material. Such compounds are stable at ordinary temperatures with respect to decomposition into their components, but melting or dissolution permits the enclosed component to escape. Examples are hydroquinone compounds which approach the composition  $(C_6H_6O_2)_x \cdot X$  ( $X = HCl, HBr, H_2S, CH_3OH, SO_2, CO_2, HCN$ , etc.); amine compounds containing sulfurous acid, e.g.  $(p-H_2NC_6H_4-NH_2)_x \cdot H_2SO_3$ ; phenol compounds, e.g.  $(C_6H_5O)_4 \cdot SO_2$ ,  $(C_6H_5O)_6 \cdot SO_2$ ,  $(C_6H_5O)_8 \cdot CO_2$ ; and certain compounds of the inert gas elements (pp. 382-383).

It is obvious that the conditions under which clathrate compounds can form are limited and highly specific. Among those of importance are:

1. An open crystal structure in the enclosing component. This necessitates directed linkages holding the molecule and crystal together, sufficient extension of the groups to form a cavity of suitable size, and a rigid structure.
2. Small access holes to the enclosed cavity. This may result from either proper disposition of groups in the formation of the crystal or sufficient surface area in the enclosing groups.
3. Ready availability of the trapped component at the time when the cavity is closed.

Such compounds are of considerable theoretical interest but are lacking in practical importance. Information on possible arrangements in clathrate compounds and the structures which lead to them is to be found in Powell's discussions.<sup>89</sup>

#### NON-STOICHIOMETRIC COMPOUNDS

The law of definite proportions is one of the basic tenets of chemistry. Its validity is indicated by the restrictions imposed upon bond formation where electrons are involved as already outlined, and its application is generally the assumed basis for any type of chemical combination. There are, however, many instances of apparent departure from this rule among *solid* compounds. Such compounds do not possess the exact compositions which are predicted from electronic considerations alone and are commonly referred to as Berthollide or non-stoichiometric compounds.

<sup>89</sup> H. M. Powell: *J. Chem. Soc.*, 1948, 61; *Endeavour*, 9, 154 (1950); *Research*, 1, 353 (1947-1948).

ric com  
compo  
such as  
 $FeO_{1.05}$   
 $Cu_{1.05}Se$   
Combin  
Lack  
defect c  
from t  
They a

1. *F*  
interst  
they v.
2. *S*  
throug  
surfac

Alth  
stoichi  
tant.  
positi  
theref  
truly  
from  
metal  
those  
know  
stoichi  
and c  
comp

Th  
cryst  
as fo  
meth  
tend  
d  
in s

Attachment page 4

*Fundamentals  
of  
chemistry  
a  
modern  
introduction*

---

FRANK BRESCIA

JOHN ARENTS

HERBERT MEISLICH

AMOS TURK

*Department of Chemistry  
The City College of the  
City University of New York*



ACADEMIC PRESS

*New York and London*

*Attachment A page 5*

*The text of this book was set in Monotype  
MODERN 8A printed and bound by The Maple Press Company.  
The book is printed on Thor Cote Plate by Bergstrom Paper  
Company. The binding is Tonero offset cloth,  
Arkwright-Interlaken Inc.  
The design of the text and cover was created by Betty Binns.  
The drawings are by F. W. Taylor.*

COPYRIGHT © 1966, BY ACADEMIC PRESS INC.

All rights reserved.

No part of this book may be reproduced in any form,  
by photostat, microfilm, or any other means, without  
written permission from the publishers.

ACADEMIC PRESS INC.

111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by

ACADEMIC PRESS INC. (LONDON) LTD.

Berkeley Square House, London W.1

*Library of Congress catalog card number: 65-26049*

First Printing, January, 1966

Second Printing, April, 1966

PRINTED IN THE UNITED STATES OF AMERICA

*Attachment A page 6*

*matter: the mass of a chemically reacting system remains constant.* This law is consistent with the data obtained with the most precise balances available. If matter is created or destroyed, the quantity is less than can be detected with the best available balance.

#### 4.2 THE LAW OF DEFINITE PROPORTIONS

Analyses of compounds show that when elements form a given compound, they always combine in the same ratio by weight. For example, independently of the source or method of formation, silicon dioxide,  $\text{SiO}_2$ , contains 46.7% by weight of silicon and 53.3% of oxygen. This knowledge is summarized in the *law of definite proportions: the weight composition of a given compound is constant.*

**EXAMPLE 1** 10.0 g of silicon dust, Si, is exploded with 100.0 g of oxygen,  $\text{O}_2$ , forming silicon dioxide,  $\text{SiO}_2$ . How many grams of  $\text{SiO}_2$  are formed and how many grams of  $\text{O}_2$  remain uncombined?

**ANSWER** Since 46.7 g of Si combines with 53.3 g of  $\text{O}_2$ , the quantity of  $\text{O}_2$  required per gram of Si is

$$\frac{53.3 \text{ g } \text{O}_2}{46.7 \text{ g Si}}$$

and, therefore, for 10.0 g of Si, the quantity of  $\text{O}_2$  required is

$$10.0 \text{ g Si} \times \frac{53.3 \text{ g } \text{O}_2}{46.7 \text{ g Si}} = 11.4 \text{ g } \text{O}_2$$

Hence, the weight of  $\text{SiO}_2$  formed is  $10.0 \text{ g} + 11.4 \text{ g} = 21.4 \text{ g}$  and the weight of uncombined  $\text{O}_2$  is  $100.0 \text{ g} - 11.4 \text{ g} = 88.6 \text{ g}$ .

#### 4.3 THE ATOMIC THEORY

The weight relationships of substances participating in chemical reactions are clearly explained in terms of the atomic theory. Although John Dalton (1803) is generally recognized as the inventor of the theory, he was anticipated by other scientists, particularly William Higgins (1789). Thus, it appears that the law of multiple proportions (Section 4.4) was foreshadowed by Higgins and Dalton from their respective atomic theories. A verified prediction made by a theory constitutes the strongest argument in its favor. However, the novel and central point of Dalton's activities was the attempt to determine the relative weights of atoms. This goal focused attention upon the theory, and revealed a new field of human endeavor that ultimately made chemistry a systematized body of knowledge.

The assumptions of the atomic theory were

- (i) *The elements are composed of indivisible particles called atoms.*
- (ii) *All the atoms of a given element possess identical properties, for example, mass.*

**ATTACHMENT B**

1. J. WATSON RESEARCH CENTER LIBRARY

# X

## TRANSPORT PROPERTIES

### A. INTRODUCTION

The principal applications of superconductors are based upon their ability to carry electric current without any loss, and therefore it is important to understand their transport properties. This chapter begins with a discussion of resistivity and critical current flow in the absence of externally applied fields. This is followed by a discussion of several techniques involving applied fields and thermal effects. The chapter concludes with sections on tunneling and the Josephson effect.

### B. CURRENT FLOW

Electric currents that flow through a superconductor owing to the action of an external source of potential are called transport currents, and those that arise in an external magnetic field to cancel the magnetic flux inside the superconductor are called diamagnetic screening currents or shielding currents. In magnet applications transport currents are started by an external source and continue to flow (persist) after its removal, while in long-distance electrical transmission applications the source voltage continues to be applied.

Current densities  $J$  are intrinsic properties and hence are more useful than currents  $I$  for quantitative comparisons between different superconductors. Transport current densities can be comparable in magnitude to shielding current densities.

The vel  
sec in the  
of the val

### 1. Resisti

A suscepti  
conductin  
resistivity,  
applicatio  
conductin  
duce shar  
diamagne  
percolatio

Many i  
temperatu  
ature and  
specimen  
made bec  
cases  $T_c$  d  
its suscep

Good c  
ties of ab  
cally decr  
mental su  
resistivit  
ments pre  
have resis  
even high  
greater th  
the semic  
these mat  
ture (cf. 1  
or 3 from

Needle  
supercon  
ature res  
supercon  
 $\text{Sr}_2\text{Cu}$   
 $\exp[(T_0/$   
tivity is  
(Kastn).

The r  
with the  
has been

The velocity of electrons at the Fermi surface  $v_F$  was estimated to be  $10^7$  cm/sec in these materials, which is of the same order as in A-15 compounds, and  $\frac{1}{10}$  of the value in aluminum (Garoc).

### 1. Resistivity

A susceptibility measurement is a better thermodynamic indicator of the superconducting state because magnetization is a thermodynamic state variable. The resistivity, on the other hand, is easier to measure, and can be a better guide for applications. The temperature of zero resistivity shows when continuous superconducting paths are in place between the electrodes. Filamentary paths can produce sharp drops in resistivity at higher temperatures than pronounced onsets of diamagnetism. This can be described in terms of two- and three-dimensional percolation thresholds (see Section III-E).

Many investigators have published figures of resistivity or resistance versus temperature, since this is the most popular way to determine the critical temperature and the sharpness of the transition. It should be remembered that if the specimen is porous, accurate determinations of the resistivity cannot readily be made because of the presence of voids and intergrain problems. In almost all cases  $T_c$  determined from the resistivity midpoint is at a higher temperature than its susceptibility counterpart.

Good conductors such as copper and silver have room-temperature resistivities of about  $1.5 \mu\Omega$  cm, and at liquid nitrogen temperature the resistivity typically decreases by a factor of 6-8, as shown by the data in Table X-1. The elemental superconductors, such as Nd, Pb, and Sn, have room-temperature resistivities a factor of 10 greater than good conductors. The other metallic elements present in oxide superconductors, namely, Ba, Bi, Ca, La, Sr, Tl, and Y, have resistivities 10-80 times that of Cu. The copper oxide superconductors have even higher room-temperature resistivities, over three orders of magnitude greater than that of metallic copper, which puts them within a factor of 3 or 4 of the semiconductor range, as shown by the data in Table X-1. The resistivity of these materials above  $T_c$  decreases more or less linearly with decreasing temperature (cf. Fig. VII-11) down to the neighborhood of  $T_c$ , with a drop by a factor of 2 or 3 from room temperature to this point, as shown by the data in the table.

Needless to say, the concept of resistivity is not a meaningful one to apply to a superconductor below  $T_c$ . Nevertheless, it is instructive to study the low-temperature resistance in nonsuperconducting compounds that are closely related to superconductors. For example, in nonsuperconducting crystals of  $(La_{1-x}Sr_x)_2(Cu_{1-y}Li_y)O_{4-\delta}$  a variable range type of hopping resistance, that is,  $R \approx \exp[(T_0/T)^4]$ , was reported. From this it has been argued that the poor conductivity is not due to a large gap, but rather to localization of the states at  $E_F$  (Kastn).

The resistivity in the high-temperature ( $80 \leq T \leq 1200$  K) region is linear with the temperature for  $T < 600$  K and superlinear above 600 K. This linearity has been linked to the two-dimensional character of the electron transport



TABLE X-1. Examples of Resistivities at Room Temperature  $\rho_{300}$ , at Low Temperature  $\rho(T)$ , and Their Ratio  $\rho_{300}/\rho(T)^a$ 

Material	$\rho_{300}$ ( $\mu\Omega$ cm)	$\rho(T)$ ( $\mu\Omega$ cm)	T (K)	$\rho_{300}/\rho(T)$	Ref.
Cu	1.68	0.18	77	9.3	
Ag	1.60	0.26	77	6.2	
Pt	10.6	1.74	77	6.1	
Sn	12.4				
Nb	12.5				
Tl	18				
Pb	20				
Sr	23				
Ca	53				
Y	57				
La	58				
Ba	60				
Bi	119				
LaSr*	2200	430	44	5.1	Kobay
	2700	850	50	3.2	Penne
	2300	510	50	4.5	Tara1
LaSr (0.05)		950( $\parallel$ )	40		Hidak
		19000( $\perp$ )	40		Hidak
(0.1)			50	3.6	Coppe
		1600	44		Kobay
LaBa(0.1)	1200		50		Tonou
YBa*	2000	1000	95	4.0	Coppe
	650	225	95	2.0	Bonn1
	900	470	100	2.9	Caval
	4000	2000	100	1.9	Mawds
		730	120	2.0	Neume
	1350	680	100	1.9	Panso
( $\rho\parallel$ )	450	200	100	2.0	Penne
( $\rho\perp$ )	13000	18000	100	2.3	Tozer
$Y_{0.6}Ba_{0.4}CuO_3$	$1.5 \times 10^6$			0.7	Tozer
DyBa*					Tonou
EuBa*	720	410	100	~1.3	Map11
TmBa*	4600	1900	100	1.8	Hikit
YbBa*				2.4	Neume
				~3.3	Map11

<sup>a</sup>Typical semiconductors have values from  $10^4$  to  $10^{15}$   $\mu\Omega$  cm and insulators range from  $10^{20}$  to  $10^{28}$   $\mu\Omega$  cm. The notation  $\parallel$  and  $\perp$  refers to resistivity measurements made parallel to and perpendicular to the Cu-O planes, respectively.

(Micna)  
mean fr  
coupling  
which w  
An ex  
observec  
trons thi  
the temp  
transitio  
the loss  
reflect th

where A  
formula  
rithmic c  
tetragon.  
also repe  
The re  
(i.e., alo  
about 20  
CuO. W  
polycryst  
Hyste  
as illustr  
for decre  
width of

## 2. Critic

When th  
current c  
effect. T  
 $J_c(O)$  at  
 $YBa_2Cu_3$   
K (e.g.,  
The v  
suring th  
sample (  
uses a  
(Kumak.

Attachment B page 3

(Micna). Applying the Mott-Ioffe-Regel rule (minimum scattering length  $<$  mean free path) to the observed normal state resistivity gave electron-phonon couplings in both LaSr\* ( $\lambda = 0.1$ ,  $\lambda_{\max} = 0.45$ ) and YBa\* ( $\lambda = 0.3$ ,  $\lambda_{\max} = 1.2$ ) which were too small to account for the observed  $T_c$  (Gurv1, Gurv2).

An exponential dependence of the resistivity of YBa\* on the temperature was observed between 80 and 1240 K (Fishe). This may occur via tunneling of electrons through barriers. The value of the exponent was different above and below the temperature  $T^*$  (700-750), which is near the tetragonal-to-orthorhombic transition. The temperature dependence of the resistivity appears to result from the loss of oxygen during heating, and the following expression was proposed to reflect this dependence:

$$\rho(T) = \frac{AT}{1 - \delta(T)} \quad (X-1)$$

where  $A$  is temperature insensitive and  $\delta(T)$  is the oxygen content factor in the formula  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (Chaki; see also Fiory). A break in the slope of the logarithmic derivative  $(T/\rho)d\rho/dT$  plotted against  $T$  occurs at the orthorhombic-to-tetragonal phase transition (Fiory). Evidence for an  $n$ -to- $p$  type transition was also reported (Choi1).

The resistivity is much higher when measured perpendicular to the  $ab$  planes (i.e., along the  $c$  axis) than it is parallel to the planes. Measured ratios  $\rho_{\perp}/\rho_{\parallel}$  are about 20 for LaSrCuO (Hidak), 50 for YBaCuO (Tozer), and  $10^5$  for BiSrCa-CuO. We see from Table X-1 that typical measured resistivities, which are on polycrystalline specimens, are much closer to the in-plane values.

Hysteresis effects have been seen in the resistance versus temperature curves, as illustrated on Fig. X-1 for  $(\text{Y}_{0.875}\text{Ba}_{0.125})_2\text{CuO}_{4-\delta}$  (Taras). The 2-K shift in  $T_c$  for decreasing and increasing temperature measurements is about half of the width of the transition.

## 2. Critical Current Density

When the current density in a superconductor exceeds a value called the critical current density  $J_c$ , the superconductivity is destroyed. This is called the Silsbee effect. The value of  $J_c(T)$  increases from zero at  $T = T_c$  to a maximum value  $J_c(0)$  at 0 K (Leide). Figure X-2 shows the magnetic field dependence of  $J_c$  for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  from 0.5 to 6 T for several temperatures in the range from 4.2 to 83 K (e.g., Panso; see also Ekinz, Jones).

The value of  $J_c$  can be determined directly by the resistivity method by measuring the current at which a small voltage (typically 1  $\mu\text{V}$ ) is induced across the sample ( $\approx 1$  cm) in a four-probe resistivity arrangement. An indirect method uses a magnetization versus field hysteresis loop through the expression (Kumak, see also Sunzz, Xiao2).

$$J_c = 30 \Delta M/d \quad \text{A/cm}^2 \quad (X-2)$$

Attachment B page 3

low

T) Ref.

1	Kobay
2	Penne
3	Tara1
	Hidak
	Hidak
5	Coppe
	Kobay
	Tonou
3	Coppe
3	Bonn1
9	Caval
9	Mawds
0	Neume
9	Panso
0	Penne
3	Tozer
7	Tozer
	Tonou
3	Map11
8	Hikit
4	Neume
3	Map11

age from  $10^{20}$  to  $10^{28}$   
o and perpendicular

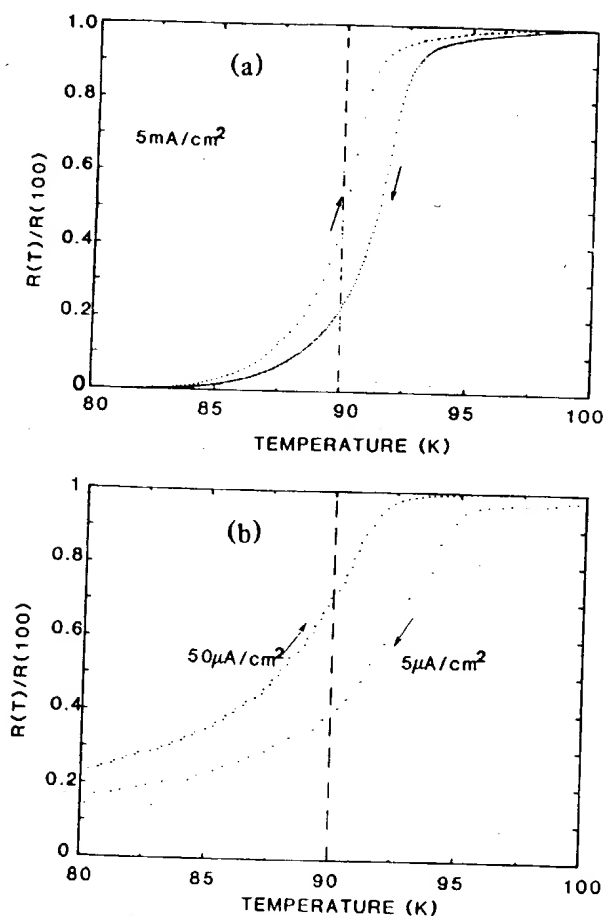


Fig. X-1. Hysteresis of resistance versus temperature for two samples of YBaCuO, for increasing and decreasing temperature, as indicated by the arrows. (a) current density  $5 \text{ mA/cm}^2$ ; (b) current density  $50 \mu\text{A/cm}^2$  for increasing temperature and  $5 \mu\text{A/cm}^2$  for decreasing temperature (Taras).

where  $\Delta M$  is the hysteresis of magnetization per unit volume in electromagnetic units per cubic centimeter and  $d$  is the size of the sample in centimeters.

The  $J_C$  values measured directly are called transport currents and those determined from hysteresis loops are called magnetization currents. Transport currents were found to be smaller than magnetization currents in the LaSrCuO (e.g., Larba) and YBaCuO (e.g., Kuma1, Togan) systems. This could be caused by granularity and intergrain contact, and improving sample quality might bring transport currents closer to their magnetization current counterparts (Wuhlz). In contrast to this, magnetization and transport critical currents of YBa\* epitaxial films were reported to be the same (Chaud, Ohzzz).

Fig. X-  
tained 1

Crit  
are list  
Umeza  
have hi  
larger  
densiti  
Jin et a  
as high  
and gr  
and sin

Gri  
apprec  
curren  
(Hueb  
Giova)

Ver  
filame  
(Chen)  
lider a  
 $10^5 \text{ A/}$   
cally s  
applic  
old on  
ity, as

Attachment B page 4

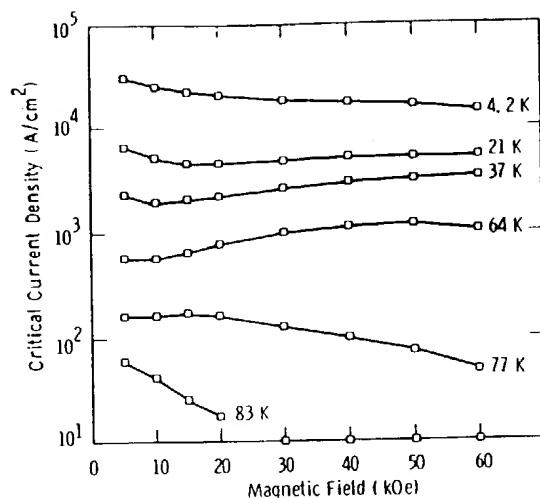


Fig. X-2. Magnetic field dependence of critical current densities of  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$  obtained from hysteresis loops (Panso) ( $10 \text{ kG} = 1 \text{ T}$ ).

Critical current densities for a number of  $\text{LaSrCuO}$  and  $\text{YBaCuO}$  materials are listed in Table X-2 (e.g., Camp1, Chau2, Chau3, Daizz, Jinz2, Kagos, Umeza, Xiao2). We see from the table that the  $\text{YBaCuO}$  compounds tend to have higher values of  $J_c$  than  $\text{LaSrCuO}$ . For the same material  $J_c$  is considerably larger at 4.2 K than at 77 K. It is also quite anisotropic, with critical current densities much larger parallel to the Cu-O planes than perpendicular to them. Jin et al. (Palca) employed a technique called melt-textured growth to achieve  $J_c$  as high as  $10^3 \text{ A/cm}^2$  in a magnetic field of 1 T at 77 K. Values of  $J_c = 10^6 \text{ A/cm}^2$  and greater have been reported in epitaxial thin films (Chaud, Kwoz1, Ohzzz) and single crystals (Crabt, Ding1, Wort1).

Grinding and heat treating samples of  $\text{LaSrCuO}$  and  $\text{YBaCuO}$  was found to appreciably increase the critical current density at 4 K (Suena). High critical currents require efficient flux pinning since  $J_c$  increases with the pinning force (Huebe, p. 125). Weak pinning leads to flux creep and low critical currents (e.g., Giova).

Very high values of  $J_c$  are needed for magnet materials. A niobium-titanium filament has been reported with  $J_c$  values as high as  $3.7 \times 10^5 \text{ A/cm}^2$  at 5 T (Cheng). The Superconducting Super Collider and Relativistic Heavy Ion Collider accelerators require 5- $\mu\text{m}$  wire filaments that support  $J_c$  of at least  $2.8 \times 10^5 \text{ A/cm}^2$  in a 5-T magnetic field (Grego). At present  $J_c$  values of technologically suitable oxide materials at 77 K are too small for such high-field magnet applications. Although the oxide superconductors do not yet compete with the old ones in critical currents, they are superior in their critical field ( $H_{c2}$ ) capability, as shown in Fig. 1-2.

Attachment B page 5

TABLE X-2. Critical Current Densities<sup>a</sup>

Compound	$J_c$ (A/cm <sup>2</sup> )	T (K)	H (T)	Measurement Method	Comments	Ref.
LaSr*	10 <sup>5</sup>	4		Mg		Suena
LaSr(0.05)	2	4.2	0.025	Tr		Larba
	1	4.2	10 <sup>-3-3</sup>	Tr		Larba
YBa*	0.75	4.2	7	Tr		Larba
	>10 <sup>6</sup>	4.2		Mg	E-film	Chaud
	>10 <sup>5</sup>	77		Mg	E-film	Chaud
	10 <sup>5</sup>	77		Mg	E-film	Chaul
	1.4 × 10 <sup>6</sup> (⊥)	5	0-1	Mg	M-xt	Crabt
	1.4 × 10 <sup>4</sup>	5	0.4	Mg	P-xt	Crabt
	1.1 × 10 <sup>4</sup> (⊥)	77	0.1	Mg	M-xt	Crabt
	4.3 × 10 <sup>3</sup> (⊥)	77	1	Mg	M-xt	Crabt
	1.2 × 10 <sup>2</sup>	77	0.6	Mg	P-xt	Crabt
	4 × 10 <sup>5</sup>	4.5		Mg	M-xt	Dingl
	3 × 10 <sup>6</sup> (⊥)	4.5		Mg	M-xt	Dingl
	>10 <sup>6</sup>	4.5	>4	Mg	M-xt	Dingl
	1-200	0	0	Tr		Ekinz
	620	77	0	Tr	$J_{c\perp}/J_{c\parallel} \sim 6$	Glowa
	3 × 10 <sup>4</sup>	77	1	Mg	sintered rod	Jinzz
	10 <sup>6</sup>	4.2		Tr	P-xt	Kumak
					E-film, bc plane	Kwozl

10 <sup>3</sup>	77		Tr	E-film, bc plane	Kwozl
1.5-2 × 10 <sup>4</sup>	4.2	1-10	Mg		Larbl
235	77	1	Mg		Larbl
10	77	6	Mg		Larbl

Attachment to page 6



### 3. Persistent Currents

The zero-resistance property of a superconductor implies that an electrical current flowing in a closed path should persist indefinitely. Several investigators have examined this property and set lower limits on the lifetime of the current and upper limits on its associated resistivity. The lifetime of the persistent or superconducting current in a cylindrical LaSrCuO sample is in excess of  $3 \times 10^6$  sec or more than a month, corresponding to a resistivity of less than  $3 \times 10^{-17} \Omega \text{ cm}$  (Wells). Current lifetimes in loops of low-temperature superconductors are much longer and suggest an effective resistivity of  $< 10^{-23} \Omega \text{ cm}$  (Chand), close to the value of  $7 \times 10^{-23} \Omega \text{ cm}$  reported for YBaCuO (Kedve). Other reported minimum resistivity determinations are:  $< 10^{-9} \Omega \text{ cm}$  (Iguch),  $4 \times 10^{-16} \Omega \text{ cm}$  for  $(\text{Y}_{0.6}\text{Ba}_{0.4})_2\text{CuO}_4$  (Skoln),  $< 10^{-16} \Omega \text{ cm}$  in YBa\* (Tjuka), and  $2 \times 10^{-18} \Omega \text{ cm}$  (Yehzz). Similar results ( $10^{-24} \Omega \text{ cm}$ ) were obtained for TlBaCaCuO.

The ceramic superconductors are granular and the relaxation of trapped field and critical current loops may be characteristic of glassy structures (cf. Section VIII-D-5). Because of the granularity even small fields can penetrate the materials. This property has been utilized to nondestructively read the supercurrent (Macfl).

## C. MISCELLANEOUS TRANSPORT PROPERTIES

In this section we will discuss some transport properties that depend upon the application of electric or magnetic fields, and some that involve thermal effects. Various transport results of YBa\*, namely, thermal conductivity, thermopower, Hall constant, and resistivity, were found to be consistent with ordinary metallic behavior with a strong phonon interaction (Uher2). It was concluded that there is no evidence for exotic electronic behavior in YBa\*.

### 1. Magnetoresistance

A number of investigators have studied the resistance versus temperature behavior in low (Hikam), high (Kwokz, Mats1, Mura1, Uher4), and very high (Ouss1) magnetic fields.

Very high field ( $H \leq 43 \text{ T}$ ) longitudinal and transverse orientation studies of YBa\* (Ouss1) show that the magnetoresistance  $\Delta\rho(T, H) = \rho(T, H) - \rho(T < 0)$  may be decomposed into three contributions

$$\Delta\rho = \Delta\rho^M + \Delta\rho^N + \Delta\rho^S \quad (\text{X-3})$$

where  $\Delta\rho^S (> 0)$  is the increase in resistance when the superconducting fluctuations are suppressed by the field,  $\Delta\rho^N$  is the normal or Lorentz magnetoresistance, and  $\Delta\rho^M$  is an unidentified component that may be associated with mag-

netic ordering at 50 K, and critical field

One of the resistivity mobility determinations in m YBaCuO systems downward to susceptibility increase in f

### 2. Hall Effect

The Hall effect in the carriers are drop to zero

In this section of the field on the an electric f The Hall co

Fig. X-3. T fields from C

Attachment B page 8

netic ordering. No change in the superconductivity was observed when  $H = 43$  T at 50 K, and only  $\approx 50\%$  normal phase resistance was found at 77 K. The upper critical field  $H_{C2}$  was estimated as  $\approx 125$  T.

One of the problems with comparing transport and magnetic  $T_c$  data is that resistivity measurements are generally made in zero magnetic field and susceptibility determinations require the presence of a field. The resistivity measurements in magnetic fields (Kobay, Wuzzz) show that for the LaSrCuO and YBaCuO systems, respectively, the transition temperature broadens and shifts downward by perhaps 1 K/T (Ihar1, Nakao), as shown in Fig. X-3. In an ac susceptibility determination a downward shift of  $T_c$  by 2 K was reported for an increase in field amplitude from 3.1 to 31  $\mu$ T (Odazz).

## 2. Hall Effect

The Hall effect provides information on the sign and the mobility of charge carriers in the normal state, and usually a positive sign indicates that the majority carriers are holes. In the superconducting state the Hall voltage is expected to drop to zero (Hundl, Zhan1).

In this experiment a magnetic field  $H_0$  is applied perpendicular to the direction of the current flow through the sample. The Lorentz force of the magnetic field on the moving charge carriers produces a charge separation which induces an electric field  $E_x$  perpendicular to the current and magnetic field directions. The Hall coefficient  $R_H$  is the ratio

$$R_H = E_x / JH_0 \quad (X-4)$$

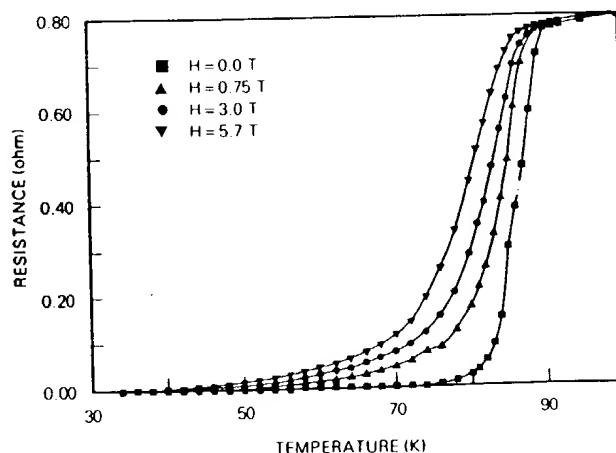


Fig. X-3. Temperature dependence of the resistance of YBaCuO in various magnetic fields from 0 to 5.7 T (Wuzzz).

Attachment B p9



where  $J$  is the current density. When the charge carriers are electrons with the density  $n$  per cubic centimeter, the Hall coefficient is negative with the value

$$R_H = -1/nec \quad (X-5)$$

in cgs units. A similar expression with a positive sign applies to hole conduction. Also of interest are the Hall mobility

$$\mu_H = R_H/\rho \quad (X-6)$$

where  $\rho$  is the resistivity, and the dimensionless Hall number  $V_0/R_{He}$ , where  $V_0$  is the volume per formula unit:

$$V_0 = 94 \text{ \AA}^3 \quad \text{for } (\text{La}_{0.925}\text{Sr}_{0.075})_2\text{CuO}_4 \quad (X-7a)$$

$$V_0 = 174 \text{ \AA}^3 \quad \text{for } \text{YBa}_2\text{Cu}_3\text{O}_7 \quad (X-7b)$$

Some authors find a strong temperature dependence of  $R_H$  or the Hall number  $V_0/R_{He}$  for  $\text{LaSrCuO}$  (Tonou) and  $\text{YBaCuO}$  (Penne, Wangz). Others find a weak dependence for  $\text{LaSrCuO}$  (Hundl, Penne, Uchi1), and a large anomaly in  $R_H$  near  $T_c$  has been observed in  $\text{YBaCuO}$  (Gottw, Yongz). Figure X-4 shows  $R_H$  of three substituted  $\text{YBaCuO}$  compounds increasing strongly with decreasing temperature (Cheon, Tana1). Figure X-5 shows the temperature dependence of the Hall mobility  $\mu_H = R_H/\rho$ , the Hall number  $V_0/R_{He}$  and the resistivity  $\rho$  of an epitaxial film of  $\text{YBaCuO}$  (Chau1, Penne). Hall-effect data on various compounds are listed in Table X-3.

Hall-effect data on  $\text{LaSrCuO}$  provided the room-temperature electron concentration  $n = 1.5 \times 10^{21}/\text{cm}^3$  and the room-temperature mobility  $\mu_H = 4.17$

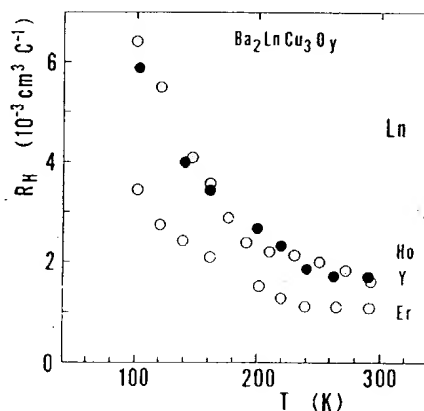


Fig. X-4. Temperature dependence of the Hall coefficient  $R_H$  of  $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$  for  $\text{Ln} = \text{Y}, \text{Ho},$  and  $\text{Er}$  (Tana1).

Attachment B page 10

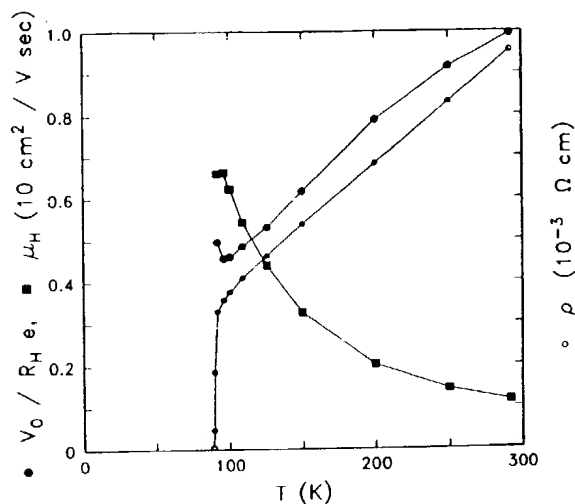


Fig. X-5. Transport data for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  showing the resistivity  $\rho$ , Hall number  $V_0/R_{He}$ , and Hall mobility  $\mu_H = R_H/\rho$  versus temperature (Chau1).

$\text{cm}^2/\text{V sec}$  (Tonou). The electron concentration decreases with increasing temperature, probably owing to significant capture of thermally excited electrons at deep traps in grain boundaries surrounding the conductive channels. The Hall coefficient measurement of  $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$  single-crystal films grown epitaxially on  $\text{SrTiO}_3$  provided a room-temperature carrier density  $n = 6.8 \times 10^{21}/\text{cm}^3$  which decreased notably with falling temperature (Suzuk).

Hall voltage measurements in  $\text{LaSr}^*$  indicated the presence of granular or inhomogeneous superconductivity (Hundl). The temperature dependence of the Hall coefficient of  $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_{4-\delta}$  was interpreted in terms of a relatively large phonon coupling and conduction via both electron and hole bands (Uher1, Uher3). The chemically determined electron deficiency or hole concentration in this compound exhibited a direct correlation with  $T_c$  for  $x \leq 0.15$ , suggestive of single-band transport and supportive of an all electronic mechanism for superconductivity (Shafe, Shaf1).

Hall-effect measurements on  $\text{YBa}_2\text{Cu}_3\text{O}_{8-\delta}$  single crystals with the magnetic field on  $\pm 1 \text{ T}$  in the  $ab$  plane yielded a negative Hall constant in the range  $-0.75$  to  $-9 \times 10^{-10} \text{ m}^3/\text{C}$  corresponding to 1.2–1.5 electrons per formula unit (Tozer). A large temperature dependence in  $R_H$  of  $\text{YBa}^*$  was attributed to multi-band conduction (Hongm) and to the temperature dependence of the 2-D and 1-D chain mobility ratio (Wangz). The Hall coefficient was inversely dependent on the temperature in the compounds  $\text{YBa}^*$  and  $\text{GdBa}^*$ , which are judged as moderately heavy Fermion-like, with a Coulomb correlation energy comparable to or larger than the bandwidths (Cheon). Around the transition a larger increase was observed in  $R_H$  for both  $\text{YBa}^*$  and  $\text{DyBa}^*$  (Yongz, Zhan1). In  $\text{DyBa}^*$  the peak in  $R_H$  corresponds to  $n \approx 4 \times 10^{19} \text{ cm}^{-3}$ , and was interpreted as a grain

TABLE X-3. Hall Effect Data<sup>a</sup>

Material	$R_H$ ( $\text{cm}^3/\text{C}$ )	$V_0/R_{He}^b$	$n$ ( $\text{cm}^{-3} \times 10^{21}$ )	$\mu$ ( $\text{cm}^2/\text{Vsec}$ )	$\rho$ ( $\mu\Omega \text{ cm}$ )	$T$ (K)	Ref.
LaSr*	+0.001 +0.004		6.0 2.1	4.3	600	300	Hundl
LaSr(0.1)		0.3		+0.75	2600	77	Ongzz
LaSrCuO	-0.005		1.5	-4.17	1200	300	Penne
La <sub>2</sub> CuO <sub>4</sub>	0.11		6.8	1.2	710	300	Tonou
YBa*	0.1			1.0	10 <sup>5</sup>	300	Suzuk
		1.0		+1.0	1000	300	Uchi2
		1.8		$\pm 0.5$	1300	300	Chau1
		1.4		$\pm 0.8$	950	300	Penne
	0.0005-0.002		1.4			290	Wangz

<sup>a</sup>Hall coefficient  $R_H$ , Hall number  $V_0/R_{He}$ , carrier density  $n$ , mobility  $\mu$ , resistivity  $\rho$ , and measurement temperature  $T$ . The notation used is: (La<sub>1-x</sub>Sr<sub>x</sub>)<sub>2</sub>CuO<sub>4</sub> = LaSr(x). LaSr(0.075) = LaSr\*, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  = YBa\*.

<sup>b</sup>Hole concentration per formula unit.

boundary  
boundary  
with decre  
change fro  
Several  
relaxation  
holelike in  
why sign c

### 3. Therm

A conduc  
steady-sta  
ture regio  
Seebeck ef  
the superc

Figure  
Seebeck co  
of  $x$  (Alle  
cient decre  
compound  
was obser  
result was  
cally to a v  
activated  
range-hop

Fig. X-6. 1  
values of  $x$

Attachment B page 12

boundary effect. In the case of  $\text{YBa}_2$ , both the intrinsic quality and the grain boundary origin were mentioned (Yongz). The Hall coefficient  $R_H$  decreases with decreasing oxygen content in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , with a plateau of very little change from  $\delta = 0.1$  to  $\delta = 0.4$  (Ongz1, Wangz).

Several papers (Allen, Alle1) have discussed the transport coefficients in the relaxation time approximation. They concluded that the Hall tensor tends to be holelike in the  $ab$  plane and electronlike in the  $ac$  and  $bc$  planes, which explains why sign differences have been reported in the literature.

### 3. Thermoelectric Effects

A conductor with a temperature gradient and no electric current develops a steady-state electrostatic potential difference between the high and low temperature regions; this phenomenon is called the thermoelectric, thermopower, or Seebeck effect. This and other related effects such as the Peltier effect vanish in the superconducting state (Hund1).

Figure X-6 shows the temperature dependence of the thermoelectric power or Seebeck coefficient  $S$  of  $\text{La}_2\text{CuO}_4$  (Gran1) and  $(\text{La}_{1-x}\text{Ba}_x)_2\text{CuO}_4$  for several values of  $x$  (Alle3, Hund1, John3, Marcu, Uchi1, Uher1, Uher2, Yanz1). The coefficient decreases with increasing  $x = 0.025, 0.05$ , and  $0.075$ , and the latter two compounds exhibit a rapid decrease to zero near the phase transition. No drop was observed in  $S$  at low temperatures for  $x = 0$ . In another study the same result was found for  $x = 0.075$ , but  $S$  for the  $x = 0$  sample decreased dramatically to a very low value below 90 K. This was attributed to a changeover from an activated type of semiconductor transport at high temperatures to a variable range-hopping type at low temperatures (Maeno).

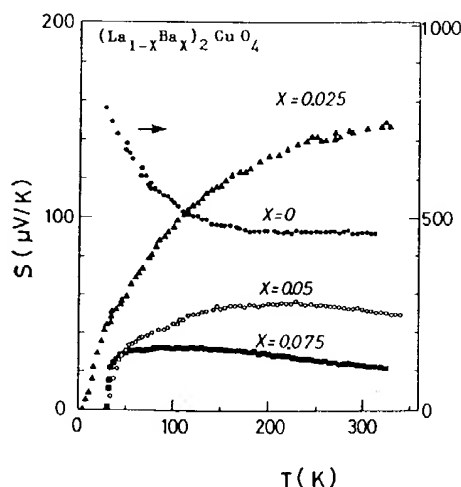


Fig. X-6. Temperature dependence of the thermopower  $S$  of  $(\text{La}_{1-x}\text{Ba}_x)_2\text{CuO}_4$  for several values of  $x$  (Uchi1).

Attachment B page 13

The thermopower of polycrystalline granular  $(\text{La}_{1-x}\text{M}_x)_2\text{CuO}_{4-\delta}$  with  $\text{M} = \text{Ba}$  or  $\text{Sr}$  was calculated in the effective medium approximation and the results for the  $x$  dependence of  $S(T)$  are in good agreement with experimental values (Xiazz). The room-temperature thermopower data of  $(\text{La}_{1-x}\text{M}_x)_2\text{CuO}_4$  fit the Heikes expression (Coope, Heike)

$$S = -\frac{k}{e} \left[ 2 \ln 2 + \ln \left( \frac{2x}{1-2x} \right) \right] \quad (\text{X-8})$$

where  $1 - 2x$  is the number of electrons per copper site. Note that this expression has no adjustable parameters.

There are reports that above  $T_c$  the thermopower in  $\text{YBaCuO}$  and its rare-earth-substituted analogues is positive (Mawds, Mitra), and also is negative (Khimz, Yaozh, Yuzzz), and examples of both cases are shown in Fig. X-7. An electronic or negative  $S(T)$  was observed in  $\text{O}_2$ -heated superconducting samples, and holelike behavior with positive  $S(T)$  was seen in air-heated nonsuperconducting ones (Raych). A sample of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$  exhibited a negative thermopower between 300 and 125 K attributed to a diffusion mechanism, a positive  $S(T)$  from 125 to 90 K ascribed to phonon drag effects, with  $S = 0$  below  $T_c = 90$  K (Yaozh; see also Khimz).

A large peak in the thermopower of  $\text{YBa}_*$ , called a precursor effect, was observed just above  $T_c$  (Mawds, Uher2). It was suggested that high- $T_c$  materials be used for thermopower test leads for the absolute determination of  $S(T)$  above the temperature range covered by the present standard Nb-Ti leads (Uherz).

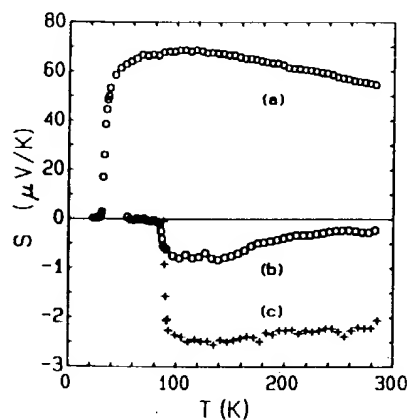


Fig. X-7. Temperature dependence of the thermopower  $S$  of (a) a ceramic sample of  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4-\delta}$ , (b) a ceramic sample of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , and (c) the  $ab$  plane of a  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  single-crystal sample. Note the different scales on the positive and negative parts of the  $y$  axis (Yuzz3).

#### 4. Photoconducti

Photoconductivity polarons and excitivity (Masum, M

#### 5. Thermal Conc

The thermal cond mal energy that is lattice (phonons) action, mean-free mal conductivity state. Thermal co talline and single of the temperatur Fig. X-8.

A detailed stu analysis of the low phonon or lattice

where

0.0

$\kappa$  ( $\text{W cm}^{-1} \text{K}^{-1}$ )

0.00

Fig. X-8. Log-log inset shows the d

Attachment B page 14

#### 4. Photoconductivity

Photoconductivity studies of LaCuO, YCuO, and YBaCuO samples suggest that polarons and excitons play a substantial role in the mechanisms of superconductivity (Masum, Masu1, Robas).

#### 5. Thermal Conductivity

The thermal conductivity  $K(T)$  is helpful in determining the fraction of the thermal energy that is transported by charge carriers and the amount carried by the lattice (phonons). It can provide information about the electron-phonon interaction, mean-free path, carrier density, and other physical properties. The thermal conductivity is not necessarily divergent or zero in the superconducting state. Thermal conductivity measurements have been reported on both polycrystalline and single-crystal samples (e.g., Bayot, More6, Uher2), and an example of the temperature dependence of  $K(T)$  in polycrystalline YBa\* is shown in Fig. X-8.

A detailed study of the transport properties of YBa\* (Gottw) included an analysis of the low-temperature ( $0.1 < T < 2$  K) behavior of  $K(T)$  in terms of a phonon or lattice contribution  $K_{ph}$  and an electronic contribution  $K_{el}$

$$K(T) = K_{ph} + K_{el} \quad (X-9)$$

where

$$K_{ph} = aT, \quad K_{el} = bT^3 \quad (X-10)$$

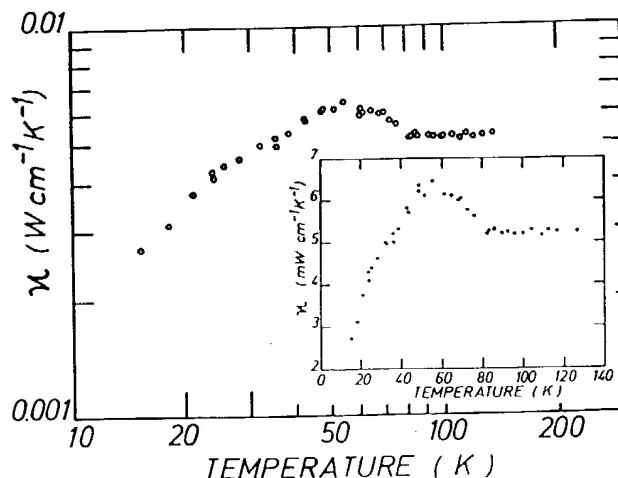


Fig. X-8. Log-log plot of the thermal conductivity of YBa\* versus the temperature. The inset shows the data replotted on a linear scale (More6).

A Hachmen + B page 15

with  $a = 16 \mu\text{W/K}^2 \text{ cm}$  and  $b = 47 \mu\text{W/K}^4 \text{ cm}$ . Hence even at  $\approx 0.1 \text{ K}$  large portions of the thermal carriers appear to be in the normal state. An observed increase in  $K(T)$  below  $T_c$  indicated large electron-phonon scattering. The authors estimated  $v_F \approx 10^7 \text{ cm/sec}$ ,  $N_{\text{eff}} \approx 10^{22}/\text{cm}^3$ , a small carrier mean-free-path, and pointed out the similarity with the heavy Fermion system  $\text{CeCu}_2\text{S}_4$ .

There was a report that  $K_{\text{el}} \ll K_{\text{ph}}$  at 300 K and  $n \approx 0.13$  carriers/Cu atom (Mori6). The observed increase in  $K(T)$  below  $T_c$  may be due to freer phonon flow, and suggests that a strong electron-phonon coupling is present in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . A  $T^3$  dependence of  $K(T)$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  below 5 K provided evidence for a temperature-independent lifetime (Herem). At 50 K the Lorentz number  $L = K\rho/T$  was estimated to be  $26 \times 10^{-8} \text{ W}\Omega/\text{K}^2$ , a factor of 20 larger than the Wiedemann-Franz value, and  $K_{\text{el}} \approx 0.1 K_{\text{ph}}$  in polycrystalline  $(\text{La}_{0.9}\text{Sr}_{0.1})_2\text{CuO}_4$  (Bartk). The thermal conductivity of sintered  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  in the temperature range from 0.1 to 10 K was linear in  $T$  at the lowest temperatures, and had a  $T^3$  dependence at the highest temperatures, in accordance with Eq. (X-9) (Graeb). This was claimed to be consistent with strong Rayleigh scattering of the phonons from the granular particles. In the  $ab$  plane single crystals of microtwinning  $\text{HoBa}_2\text{Cu}_3\text{O}_{7-x}$  obeyed a power law  $K(T) = aT^n$  with  $n \approx 2$ , a behavior similar to that observed in glasses (Graeb).

#### D. TUNNELING PROPERTIES

Tunneling can be carried out through an insulating layer, I, between two superconductors (S-I-S), between a superconductor and a normal material (S-I-N), and between two normal materials (N-I-N) such as two semiconductors. The dc and ac Josephson effects involve particular types of tunneling phenomena across a barrier between two superconductors. The SQUID is an application of Josephson tunneling that involves macroscopic quantum phenomena. These topics will be discussed in the following three sections.

One of the preferred ways to measure an energy gap is through tunneling experiments, and many values of the gap energy determined by this technique are recorded in Table IX-1.

##### 1. Tunneling Measurements

A tunneling study of  $\text{LaSrCuO}$  thin films was made using both the sandwich-type and the point-contact-type tunneling techniques (Naito). Sandwich-type junctions were prepared by forming a small window  $\approx 150 \mu\text{m}$  square and depositing a Pb counter electrode, which formed a natural high-resistance tunnel barrier, typically  $1 \text{ M}\Omega$ . Point contact tunneling was done with the aid of a scanning electron microscope (SEM) using a tungsten probe with a tip radius less than 100 nm. Continuous scanning was not possible, but several points on the same specimen within a  $1 \times 1 \mu\text{m}^2$  window could be sampled. The curves of differential tunneling conductances  $dI/dV$  as a function of the bias voltage presented in Fig.

X-9 have ordinary gap energies

In a low-temperature electrons tunneling experiments in terms of the grain sizes  $\leq$  study of  $(\text{Y}_0)$  provided gap ratio (Ekino) tunneling current niobium tip (Gall1).

Electron tunneling differential resistance not appear in

Fig. X-9. Point contact tunneling at 4.2 K (Naito)

Attachment B page 16

X-9 have ordinate scales proportional to the density of states, and they provide gap energies.

In a low-temperature SEM tunneling study of  $(\text{La}_{0.9}\text{Sr}_{0.1})_2\text{CuO}_{4-\delta}$  at 5 K the electrons tunneled from the tip into many superconducting grains with inhomogeneities small compared to the grain sizes (Kirtl). The data were analyzed in terms of the model of Zeller and Giaever (Zelle), and gave  $E_g/kT_c$  in the range from 3.5 to 6.3. Another experiment (Tsuei) was consistent with tunneling into grain sizes  $\leq 1$  nm which are much smaller than the apparent crystal sizes. A study of  $(\text{Y}_{0.55}\text{Ba}_{0.45})_2\text{CuO}_{4-\delta}$  using point-contact tunneling at 4.2 and 27.4 K provided gap ratios  $E_g/kT_c$  in the range 3.8–4.2, somewhat larger than the BCS ratio (Ekino). Figure X-10 shows an example of the way  $I$  versus  $V$  SEM electron tunneling curves give a range of gap values ( $5 \text{ meV} \leq E_g \leq 190 \text{ meV}$ ) for a niobium tip located at various points of an aluminum-doped YBa\* sample (Gall1).

Electron tunneling between the grains of oxygen-poor YBa\* exhibited a differential resistance  $dV/dI$  which appears to have an asymptotic peak that did not appear in homogeneous oxygenated samples (Escud). The gap signature was

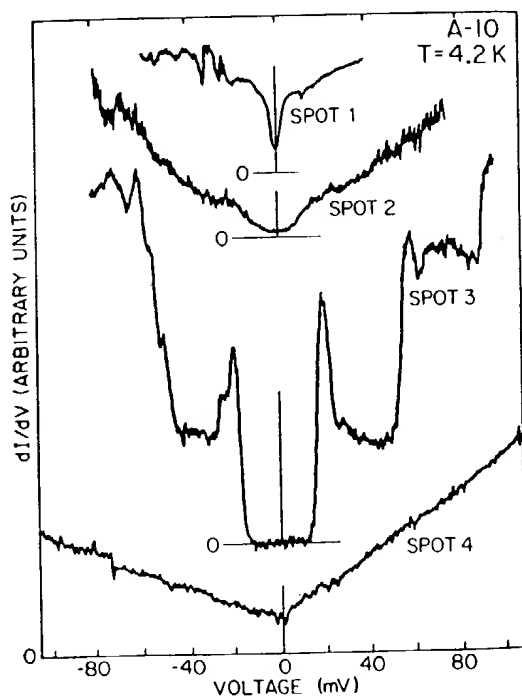


Fig. X-9. Point-contact tunneling conductance for four locations on a LaSrCuO thin film at 4.2 K (Naito).

Attachment B page 17



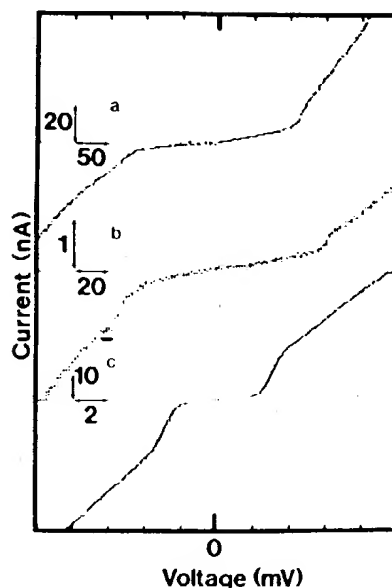


Fig. X-10. Current versus voltage plots obtained using a niobium tip at different positions on the surface of aluminum-doped  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . The difference scales used for each curve are indicated. The spectra from top to bottom show jumps in current at 95, 30, and 2.5 meV, respectively (Gall1).

not very well resolved and  $E_g/kT_c \approx 7-13$ . Tunneling studies of  $\text{YBa}^*$  thin films (Ogale) exhibited a dependence of the normalized critical current  $I_c/I_{c0}$  on  $T/T_c$ , which differs from some recent S-I-S junction calculations (Ambeg). The deGennes model was reported to be better over a small temperature range, but the predicted curvature was larger than that of the data.

In the break-junction tunneling technique (More3, More5) a small piece of bulk material is electromechanically broken under liquid helium, and the freshly fractured surfaces are adjusted to form a tunneling barrier with the liquid helium acting as the insulator (More4). The most common current-voltage curves obtained by this technique (More4) closely followed a quadratic current dependence on the voltage. Some curves have derivatives that exhibit structure indicative of the presence of gap sum voltages, and others have shapes that suggest quasi-particle tunneling between superconducting electrodes (More1). Related behaviors are observed, for example, for tunneling from a PtIr tip into  $\text{LaSrCuO}$  (Tsuei, Zelle).

In the absence of high-quality "sandwich" junctions these break-junction results are interesting. However, the effects of the strain and elastic failure on the electronic properties of the specimens and junctions is not clear. This could be of concern, particularly in the case of ceramic superconductors that are sensitive to sample treatment.

## 2. Josephs

When two electron p: other. The

1. The across the  $\delta$  is a phas
2. The  $\sin[\delta - (4$   $h$  is the fr
3. Mac with an os

where the magnetic fluxoid on

In the unbiased diatively Wengl). percondu

Anom field stre was 20 m above 56 were mo. to flux j have tra

Super a few mi could ca tum vol junction can pre voltages junction Josep bounda

## 2. Josephson Effect

When two superconductors are separated by a thin layer of insulating material, electron pairs can tunnel through the insulator from one superconductor to the other. There are three effects of pair tunneling, namely:

1. The dc Josephson effect, which is the flow of a dc current  $J = J_0 \sin \delta$  across the junction in the absence of an applied electric or magnetic field, where  $\delta$  is a phase factor and  $J_0$  is the maximum zero voltage current.
2. The ac Josephson effect relates to the flow of a sinusoidal current  $J = J_0 \sin[\delta - (4\pi e V t/h)]$  across a junction with an applied voltage  $V$  where  $\nu = 2eV/h$  is the frequency of oscillation.
3. Macroscopic quantum interference effects involving a tunneling current  $J$  with an oscillatory dependence on the applied field, given by

$$J = J_0 \frac{\sin \pi \Phi / \Phi_0}{\pi \Phi / \Phi_0} \quad (\text{X-11})$$

where the magnetic flux  $\Phi$  may be approximated as the product of the average magnetic field strength times the cross-sectional area, and  $\Phi_0 = hc/2e$  is the fluxoid or quantum of magnetic flux.

In the reverse ac Josephson experiment, dc voltages are induced across an unbiased junction by introducing an rf current into the junction, or by radiatively coupling an rf signal through a coil surrounding the sample (Chenz, Weng1). It was suggested that this result supports the existence of granular superconductivity in YBaCuO at 240 K (Weng1).

Anomalous voltage excursions as a function of temperature and magnetic field strength were reported above 100 K (Caizz). The onset of the excursions was 20 mT, they reached a maximum at about 33 mT, and disappeared for fields above 56 mT. The voltage jumps were different for cooling and heating, and they were more frequent for larger samples. These transient voltages were attributed to flux jumps of granular superconductors. It was proposed that some grains have transition temperatures as high as 160 K.

Superconducting oxide materials are porous with chains of grains measuring a few microns in size. Owing to the inverse Josephson effect an applied rf current could cause individual Josephson junctions in these materials to develop quantum voltages given by  $V_j = nh\nu/2e$ , which is on the order of nanovolts. Such junctions could even be inside the grains themselves (Blaze). Thermal smearing can prevent the detection of individual quantum voltages, but observable dc voltages in the millivolt range can result from the summation of thousands of junctions with  $n$  values as large as 100.

Josephson junctions in thin films of LaSr(0.1) are believed to form at grain boundaries. In one experiment the Josephson current was found to be propor-

Attachment B page 1.9

tional to  $[1 - (T/T_c)]^2$ . In contrast, samples of YBa\* (Cuizz) and  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  (Suzu2) produced current proportional to  $[1 - (T/T_c)]^{3/2}$ , which may suggest proximity effects (Fuku3, Kobes, Kres3, Lynto) with comparatively long-range leakage of Cooper pairs (Moriw). The proximity effect can cause two superconductors with different  $T_c$  values in contact with each other to exhibit one intermediate  $T_c$ , and it can cause a nonsuperconductor-superconductor pair to act like a superconductor with a lower  $T_c$  (Kres3).

A LaSr\* sample mounted in a point contact current-voltage probe with a conducting tip produced a hysteretic  $I$  versus  $V$  characteristic of the type shown in Fig. X-11 (Estev, Tsaiz). Microwave irradiation produced the Shapiro steps (Baron), which result from the beating of the oscillating Josephson supercurrent with the microwaves. The separation in voltage between these steps is proportional to the microwave frequency, and their amplitude is Bessel-like. The Josephson junction characteristics are observed even when the metal tip is non-superconducting, which indicates that the superconducting junction is inside the material under the tip (Estev). The absence of voltage steps during the microwave irradiation of a Nb-YBaCuO point-contact junction suggests that the coupling between the superconducting regions along the percolative path is non-Josephson (Tsaiz). Other workers studying Nb-YBa\* point-contact junctions observed Shapiro steps and an unusual noise behavior along the  $I$ - $V$  characteristic (Kuzni), and an estimate was made of  $\Delta \approx 19.5 \pm 20$  mV and  $2\Delta/kT_c \approx 4.8$  (Baro1). Very clear steps were observed in a weak link fabricated by carving a bridge ( $0.1 \times 0.2$  mm<sup>2</sup>) in a  $10 \times 2 \times 2$  mm<sup>3</sup> YBa\* sample. Both harmonic ( $n\Phi_0$ ) and subharmonic ( $n\Phi_0/m$ ) flux quantum steps were reported at 77 K (Chan2). Other microwave radiation experiments have also been carried out (McGra, Nieme, Mengz).

Theoretically microwave absorption by S-I-S junctions with square-well potentials at low temperatures is calculated to occur in sharp steps whenever the microwave energy is an integral multiple of the minimum energy needed to excite quasi particles from the ground state to bound Andreev excited states (Aberl, Andre). Andreev reflections at an Ag-YBa\* interface on a thin film have been reported. It was argued to provide evidence for Cooper or zero-momentum carrier pairs. The gap as determined from the reflection data was 12.5 meV, compared with 14 meV deduced from tunneling on the same film. These results are consistent with a BCS picture (Hoeve).

### 3. Macroscopic Quantum Phenomena

Macroscopic quantum phenomena were reported in Sn-YBaCuO and YBaCuO-YBaCuO point contacts. The critical current and the voltage are periodic in the magnetic field, and for each voltage there is a minimum and a maximum value of the current between which the oscillations take place when the magnetic field is varied (DeWae, DeWa1). This dc SQUID (Finkz, Jakle, Soule) behavior has been observed up to 40 K (Kawab), 66 K (DeWae, DeWa1), and 90 K (Tsail).

Fig. X-  
with a  
trace. 1  
(b) Ste

SQ  
The fl  
(Goug  
sampl  
operat  
 $T/\sqrt{H}$   
than t

Attachment B page 20

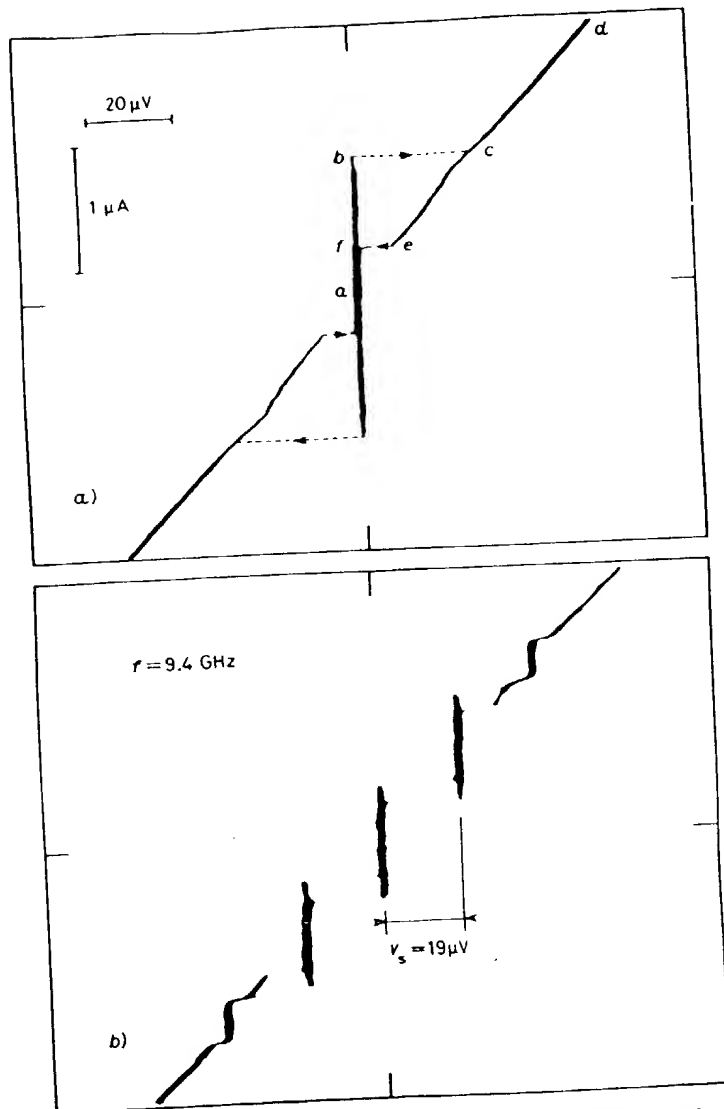


Fig. X-11. (a) Oscilloscope trace of a current-voltage characteristic obtained at 4.2 K with an aluminum tip on a LaSr\* sample. Letters *a* through *f* indicate the sense of the trace. Dashed lines have been added to indicate the switching between the two branches. (b) Steps induced by microwave irradiation at the frequency  $f = 9.4$  GHz (Estev).

SQUIDS have been fabricated from  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (Colcl, Kawab, Zimme). The flux quantum  $\Phi_0$  obtained from these devices was the expected  $hc/2e$  (Gough, Koch1, Koch2). For a YBa\* specimen to exhibit SQUID behavior the sample need not necessarily be multiply connected. For such a YBa\* SQUID operating in the magnetometer mode the field spectral density was  $5.8 \times 10^{-10} T/\sqrt{H_C}$  at 4.2 K and  $1.5 \times 10^{-10} T/\sqrt{H_C}$  at 77 K (Pegru). This value is better than that of a good flux-gate magnetometer.

Attachment B page 21

**ATTACHMENT C**

(V)

NATIONAL SCIENCE FOUNDATION  
WASHINGTON, D.C. 20550

Dear Drs. Bednorz + Müller.

12/3/86

This is just to inform you that my group  
at the U. of Houston has reproduced your  
results (Z. Phys. B 64, 189 (86)) three weeks ago.

A small ac diamagnetic signal was also  
detected. Magnetic field was found to suppress  
the transition. I believe that it is superconductivity.  
Now the question is "what phase" or "mixed  
phases". Soon, you will hear from us more.

Please send me more information!

Sincerely yours

my phone:  
(202) 357-9737  
or  
(713) 747-2842  
your phone No.?

C. W. Chu  
(also Physics, U. of Houston)  
Houston, TX 77004

P.S. Currently, I am the Director of Solid Physics Program  
at the National Science Foundation

Attachment C

OO-IBM YORKTOWN

	DATE	TIME	TO/FROM	MODE	MIN/SEC	PGS	CMD#	STATUS
32	06/24	17:50	7033057718	EC--S	03'37"	020	017	OK

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: June 24, 1999

Serial No. 08/303,561

Group Art Unit: 1105

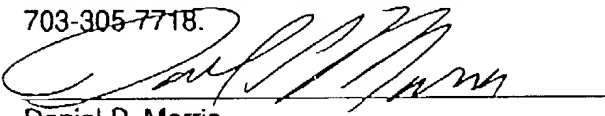
Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

**CERTIFICATE OF FACSIMILE TRANSMISSION**

I hereby certify that this paper is being facsimile transmitted under Rule CFR 1.61(d) to the U.S. Patent and Trademark Office on the date shown above To telephone number 703-305-7718.

  
Daniel P. Morris  
Reg. No. 32,053

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

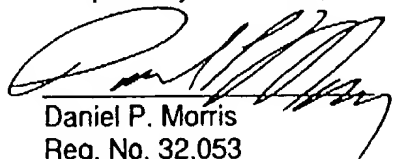
**Response After Final Rejection**

In response to the final rejection dated June 25, 1998 please consider the following:

**REMARKS**

On December 27, 198, applicants submitted by facsimile transmission the attached Amendment After Final Rejection Under 37 CFR 1.116. Attached is the facsimile machine transmission status report recording that 18 pages were successfully transmitted to telephone number 703-305-3599.

Respectfully submitted,

  
Daniel P. Morris  
Reg. No. 32,053  
(914) 945-3217

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: June 24, 1999

Serial No. 08/303,561

Group Art Unit: 1105

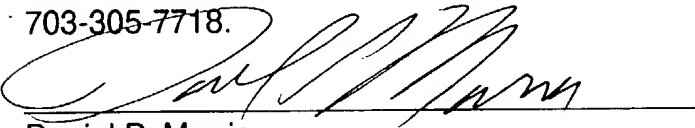
Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

**CERTIFICATE OF FACSIMILE TRANSMISSION**

I hereby certify that this paper is being facsimile transmitted under Rule CFR 1.61(d) to the U.S. Patent and Trademark Office on the date shown above To telephone number 703-305-7718.

  
Daniel P. Morris  
Reg. No. 32,053

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

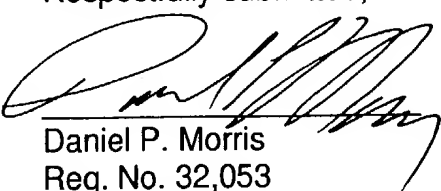
**Response After Final Rejection**

In response to the final rejection dated June 25, 1998 please consider the following:

**REMARKS**

On December 27, 1998, applicants submitted by facsimile transmission the attached Amendment After Final Rejection Under 37 CFR 1.116. Attached is the facsimile machine transmission status report recording that 18 pages were successfully transmitted to telephone number 703-305-3599.

Respectfully submitted,

  
Daniel P. Morris  
Reg. No. 32,053  
(914) 945-3217



IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598

	DATE	TIME	TO/FROM	MODE	MIN/SEC	PGS	CMD#	STATUS
11	12/27	01:36	917033053599	EC--S	03'57"	018	145	OK

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 27, 1998

Serial No. 08/303,561

Group Art Unit: 1105

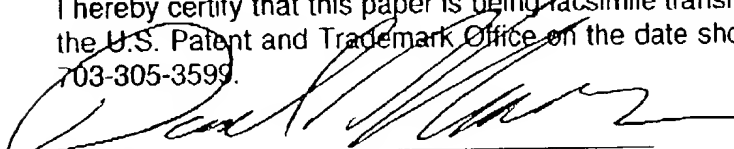
Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

I hereby certify that this paper is being facsimile transmitted under Rule CFR 1.61(d) to  
the U.S. Patent and Trademark Office on the date shown above to telephone number  
703-305-3599.

  
Daniel P. Morris  
Reg. No. 32,053

**AMENDMENT AFTER FINAL REJECTION UNDER 37 CFR 1.116**

Sir:

In response to the Office Action dated June 25, 1998, please consider the following:

**REMARKS**

Applicants' claims have been rejected under 35 USC 112 as indefinite for using the  
terminology "perovskite-like" and "rare-earth-like". Applicants respectfully disagree.

In addition to the evidence previously submitted showing that these are terms used by  
persons of skill in the art and that there are issued patents containing these terms in  
the claims which shows that the USPTO recognizes these terms as definite under 35

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 27, 1998

Serial No. 08/303,561

Group Art Unit: 1105

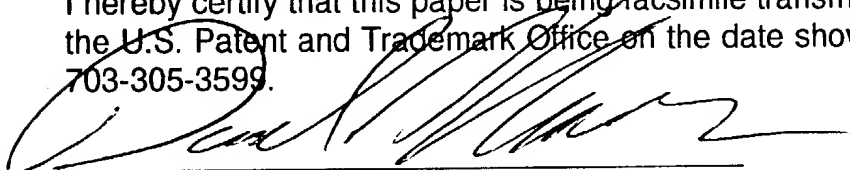
Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

I hereby certify that this paper is being facsimile transmitted under Rule CFR 1.61(d) to the U.S. Patent and Trademark Office on the date shown above to telephone number 703-305-3599.



Daniel P. Morris  
Reg. No. 32,053

**AMENDMENT AFTER FINAL REJECTION UNDER 37 CFR 1.116**

Sir:

In response to the Office Action dated June 25, 1998, please consider the following:

**REMARKS**

Applicants' claims have been rejected under 35 USC 112 as indefinite for using the terminology "perovskite-like" and "rare-earth-like". Applicants respectfully disagree.

In addition to the evidence previously submitted showing that these are terms used by persons of skill in the art and that there are issued patents containing these terms in the claims which shows that the USPTO recognizes these terms as definite under 35

USC 112, applicants submit the following additional evidence that the USPTO recognizes these terms as definite under 35 USC 112.

The undersigned attorney did a search in Lexis for the terms "like" in issued US patents. As shown in Attachment A, this search Lexis found 140,058 issued US patents using the terminology "like" in the claims. The USPTO has, therefore, accepted this terminology as definite within the meaning of 35 USC 112. A number of specific examples are provided in Attachments B to J, each of which are the results of a similar Lexis search. (Lists of the patent numbers will be provided at the request of the examiner.) Attachment B shows that there are 443 issued US patents having the term "diamond like" in the claims. Attachment C shows that there are 319 issued US patents having the term "diamond like carbon" in the claims. Attachment D shows that there are 10 issued US patents having the term "halogen like" in the claims. Attachment E shows that there are 11 issued US patents having the term "oxygen like" in the claims. Attachment F shows that there are 79 issued US patents having the term "ceramic like" in the claims. Attachment G shows that there are 31 issued US patents having the term "carbon like" in the claims. Attachment H shows that there are 5 issued US patents having the term "silicon like" in the claims. Attachment I shows that there are 10 issued US patents having the term "nitrogen like" in the claims. Attachment J shows that there are 17 issued US patents having the term "copper like" in the claims. In view thereof applicants respectfully request the examiner to withdraw the rejection of their claims as indefinite for using the terminology "perovskite like" and "rare-earth-like" since use of the term "like" is recognized as definite under 35 USC 112 by the USPTO.

Applicants claims have been rejected under 35 USC 102(a) and 103 over the Asahi Shinbum article which has a date of Nov. 28, 1986. In addition to evidence previously submitted proving that applicants conception was in the United States at applicants direction prior to Nov. 28, 1986 applicants submit the following additional evidence. Attachment K page 1 is a copy of the front cover of Zeitschrift Fur Physik B Condensed Matter Vol. 64 which contains the article ( pp 189-193) referred to and incorporated by reference at page 6, lines 6-10, of applicant's specification which applicants state is "[t]he basis or our invention". This page bears in the upper right the date stamp of the IBM Research Library bearing the date of Sept. 18, 1986. Page 2 of Attachment K is an enlarged view of the upper right corner showing the date stamp. Thus the assignee of the present invention IBM, the employer of the inventors at the time of the conception of the invention, had in its possession in the United States a copy of the article which applicants state forms the basis of their invention prior to the date of the Asahi Shinbum. Thus IBM had in its possession in the United States a written description of applicants' invention in "ready to patent form" as defined by the United States Supreme Court in Pfaff v. Wells No. 97-1130 decided November 10, 1998 prior to the date of the Asahi Shinbum article. The US Supreme Court held that "reduction to practice" is not needed to establish a date for invention. The court stated " [t]he statute's only specific reference to that term is found in §102(g), which sets fort the standard for resolving priority between two competing claimants to a patent." Since §102(g) is not applicable here, "diligence" and "reduction to practice" are not required. Applicants article in Zeitschrift Fur Physik "is proof that prior to [the date of the Asahi

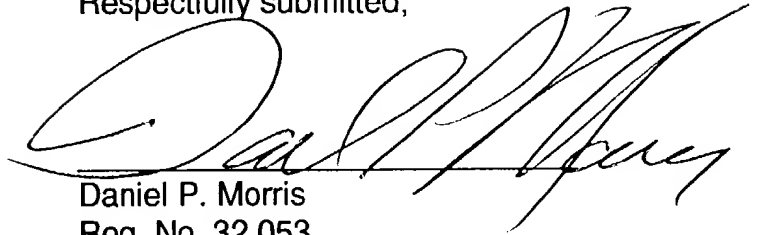
Shinbum article applicants have] prepared drawings or other descriptions of the invention that were sufficiently specific to enable a person skilled in the art to practice the invention." The Asahi Shinbum article states that applicants' work was reproduced, by others, thus applicants article was specifically specific for a person of skill in the art to practice applicants' invention. Also, as stated in a prior response , more than 5,200 articles refer to applicants article showing that applicants enabled the field of high Tc superconductivity In view of applicants remarks the examiner is respectfully requested to withdraw the rejection of applicant's claims under 35 USC 102(a) and 103 as unpatentable over the Asahi Shinbum article.

In addition to the evidence previously submitted in support of applicants position that their claims are fully enabled, applicants refer to the book "Structural Inorganic Chemistry", A. F. Wells, Oxford At the Clarendon Press (1962) which provides teaching of the general principles of ceramic science and the structure and properties of perovskite materials.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

If the above-identified Examiner's Action is a final Action, and if the above-identified application will be abandoned without further action by applicants, applicants file a Notice of Appeal to the Board of Appeals and Interferences appealing the final rejection of the claims in the above-identified Examiner's Action. Please charge deposit account 09-0468 any fee necessary to enter such Notice of Appeal.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Daniel P. Morris", written over a horizontal line.

Daniel P. Morris  
Reg. No. 32,053

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598  
(914) 945-3217

CLAIMS (LIKE)

Your search request has found 140,058 PATENTS through Level 1.  
To DISPLAY these PATENTS press either the KWIC, FULL, CITE or SEGMENTS key.  
To MODIFY your search request, press the M key (for MODIFY) and then the ENTER key.

For further explanation, press the H key (for HELP) and then the ENTER key.

Attachment A



CLAIMS (DIAMOND LIKE)

Your search request has found 443 PATENTS through Level 1.  
To DISPLAY these PATENTS press either the KWIC, FULL, CITE or SEGMENTS key.  
To MODIFY your search request, press the M key (for MODIFY) and then the ENTER key.

For further explanation, press the H key (for HELP) and then the ENTER key.

Attachment B

DATE: DECEMBER 26, 1998  
CLIENT: 074  
LIBRARY: LEXPAT  
FILE: UTIL

Your search request is:  
CLAIMS(DIAMOND LIKE CARBON)

Number of PATENTS found with your search request through:  
LEVEL 1... 319

To display the next screen of text of the PATENT you were viewing, press the  
NEXT PAGE key.

To redisplay the screen of text of the PATENT you were viewing, press the  
ENTER key.

For further explanation, press the H key (for HELP) and then the ENTER key.

Attachment C

CLAIMS (HALOGEN LIKE)

Your search request has found 10 PATENTS through Level 1.  
To DISPLAY these PATENTS press either the KWIC, FULL, CITE or SEGMENTS key.  
To MODIFY your search request, press the M key (for MODIFY) and then the ENTER key.

For further explanation, press the H key (for HELP) and then the ENTER key.

Attachment D

CLAIMS (OXYGEN LIKE)

Your search request has found 11 PATENTS through Level 1.  
To DISPLAY these PATENTS press either the KWIC, FULL, CITE or SEGMENTS key.  
To MODIFY your search request, press the M key (for MODIFY) and then the ENTER key.

For further explanation, press the H key (for HELP) and then the ENTER key.

Attachment E

CLAIMS (CERAMIC LIKE)

Your search request has found 79 PATENTS through Level 1.  
To DISPLAY these PATENTS press either the KWIC, FULL, CITE or SEGMENTS key.  
To MODIFY your search request, press the M key (for MODIFY) and then the ENTER key.

For further explanation, press the H key (for HELP) and then the ENTER key.

Attachment

CLAIMS (SILICON LIKE)

Your search request has found 5 PATENTS through Level 1.  
To DISPLAY these PATENTS press either the KWIC, FULL, CITE or SEGMENTS key.  
To MODIFY your search request, press the M key (for MODIFY) and then the ENTER key.

For further explanation, press the H key (for HELP) and then the ENTER key.

Attachment H

CLAIMS (CARBON LIKE)

Your search request has found 31 PATENTS through Level 1.  
To DISPLAY these PATENTS press either the KWIC, FULL, CITE or SEGMENTS key.  
To MODIFY your search request, press the M key (for MODIFY) and then the ENTER key.

For further explanation, press the H key (for HELP) and then the ENTER key.

Attachment G

CLAIMS (NITROGEN-LIKE)

Your search request has found 10 PATENTS through Level 1.  
To DISPLAY these PATENTS press either the KWIC, FULL, CITE or SEGMENTS key.  
To MODIFY your search request, press the M key (for MODIFY) and then the ENTER key.

For further explanation, press the H key (for HELP) and then the ENTER key.

Attachment I



CLAIMS (COPPER LIKE)

Your search request has found 17 PATENTS through Level 1.  
To DISPLAY these PATENTS press either the KWIC, FULL, CITE or SEGMENTS key.  
To MODIFY your search request, press the M key (for MODIFY) and then the ENTER key.

For further explanation, press the H key (for HELP) and then the ENTER key.

Attachment J

# Condensed Matter

## Zeitschrift für Physik B

Volume 64 Number 2 1986



European Physics Journal

A 20350 D

- |  |     |   |     |
|--|-----|---|-----|
| <i>P. Marksteiner, P. Blaha, K. Schwarz</i><br>Electronic Structure and Binding Mechanism of $\text{Cu}_2\text{O}$   | 119 | <i>R. Bayerer, J. Heber, D. Mateika</i><br>Crystal-Field Analysis of $\text{Tb}^{3+}$ Doped Yttrium Aluminium<br>Garnet using Site-Selective Polarized Spectroscopy   | 201 |
| <i>R.D. Williams, S.W. Lovesey, W. Renz</i><br>Scattering Response of a Phonon Damped<br>Harmonic Oscillator   | 129 | <i>S. Lipiński, H. Capellmann</i><br>On the Magnetization Fluctuations in the<br>Completely Disordered Paramagnetic Medium  | 211 |
| <i>Ch. Zeller, G. Abstreiter</i><br>Electric Subbands in Si/SiGe Strained Layer<br>Superlattices   | 137 | <i>G. Moro, P.L. Nordio</i><br>Rotational Diffusion in Cubic Fields   | 217 |
| <i>J. Mašek</i><br>Electronic States in Disordered Systems with Statistical<br>Correlations: Self-Consistent Born Approximation  | 145 | <i>K.P. Ghatak, M. Mondal</i><br>Theoretical Analysis of the Gate Capacitance in<br>$n$ -Channel Inversion Layers on Ternary Chalcopyrite<br>Semiconductors in the Presence of a Quantizing<br>Magnetic Field | 223 |
| <i>E. Bauer, E. Gratz, H. Nowotny</i><br>Transport Properties and Electronic Structure of<br>Nonmagnetic REAg Compounds  | 151 | <i>P.M. Lam</i><br>Corrections to Scaling for Branched Polymers   | 227 |
| <i>K. Winzer</i><br>Temperature- and Magnetic Field Dependence of the<br>Hall Effect in the Heavy Fermion System $\text{CeCu}_6$   | 159 | <i>C.M. Arizmendi, L.N. Epele, H. Fanchiotti,<br/>C.A. García Canal</i><br>Ferromagnetic and Antiferromagnetic Properties of<br>the Blume-Capel Model in (1+1) and (2+1)<br>Dimensions                        | 231 |
| <i>K.D. Schotte, D. Förster, U. Schotte</i><br>Can Ultrasonic Sound Attenuation Measurements<br>Elucidate the Coupling of "Heavy Electrons" to the<br>Lattice?   | 165 | <i>E. Freidkin, P.S. Riseborough, P. Hänggi</i><br>Quantum Tunneling at Low Temperatures: Results<br>for Weak Damping   | 237 |
| <i>M. Yoshizawa, B. Lüthi, K.D. Schotte</i><br>Grüneiser: Parameter Coupling in Heavy Fermion<br>Systems   | 169 | <i>G. Hu</i><br>A Comparison of Master Equation and Fokker-<br>Planck Equation in the Thermodynamic Limit   | 247 |
| <i>F. Gross, B.S. Chandrasekhar, D. Einzel, K. Andres,<br/>P.J. Hirschfeld, H.R. Ott, J. Beuers, Z. Fisk, J.L. Smith</i><br>Anomalous Temperature Dependence of the Magnetic<br>Field Penetration Depth in Superconducting $\text{UBe}_{13}$ | 175 | <i>J. Honerkamp, A. Baumgärtner</i><br>Anomalous Diffusion on a Fractal: A First Passage<br>Time Problem  | 253 |
| <i>J.G. Bednorz, K.A. Müller</i><br>Possible High $T_c$ Superconductivity in the<br>$\text{Ba-La-Cu-O}$ System   | 189 | Indexed in <i>Current Contents</i>  |     |
| <i>R. Bayerer, W. Schneider, J. Heber, D. Mateika</i><br>Electron-Phonon Relaxation in $^5\text{D}_4$ of $\text{Tb}^{3+}$ in<br>Yttrium Aluminium Garnet   | 195 | Evaluated and abstracted for PHYS on STN  |     |



Springer International

Attachment K page 1

inse  
1a1te

Attachment K page 2

OO-IBM YORKTOWN

	DATE	TIME	TO/FROM	MODE	MIN/SEC	PGS	CMD#	STATUS
17	06/15	10:41	7033057718	EC--S	02'57"	015	245	OK

---

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: June 15, 1999

Serial No. 08/303,561

Group Art Unit: 1105

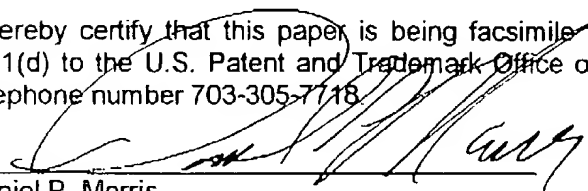
Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

**CERTIFICATE OF FACSIMILE TRANSMISSION**

I hereby certify that this paper is being facsimile transmitted under Rule CFR 1.61(d) to the U.S. Patent and Trademark Office on the date shown above To telephone number 703-305-7718.

  
Daniel P. Morris  
Reg. No. 32,053

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**Amendment After Final Rejection**

In response to the final rejection dated June 25, 1998 please consider the following:

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: June 15, 1999

Serial No. 08/303,561

Group Art Unit: 1105

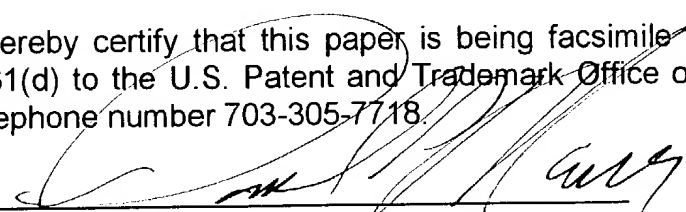
Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

**CERTIFICATE OF FACSIMILE TRANSMISSION**

I hereby certify that this paper is being facsimile transmitted under Rule CFR 1.61(d) to the U.S. Patent and Trademark Office on the date shown above To telephone number 703-305-7718.

  
\_\_\_\_\_  
Daniel P. Morris  
Reg. No. 32,053

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**Amendment After Final Rejection**

In response to the final rejection dated June 25, 1998 please consider the  
following:

## IN THE CLAIMS

Added claims:

143. (Added) A method, comprising the steps of:

forming a composition including a transition metal, a group IIIB element, an alkaline earth element, and oxygen, where said composition is a mixed transition metal oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K,

maintaining said composition in said superconducting state at a temperature greater than 26°K, and

passing an electrical current through said composition while said composition is in said superconducting state.

144. (Added) The method of claim 143, where said transition metal is copper.

145. (Added) A superconductive method for causing electric current flow in a superconductive state at a temperature in excess of 26 K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the composition having a superconductor transition temperature  $T_c$  of greater than 26 K;

(b) maintaining the superconductor element at a temperature above 26 K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

146. (Added) The superconductive method according to claim 145 in which the copper-oxide compound of the superconductive composition includes at least one element selected from the group consisting of a rare-earth element and a Group III B element and at least one alkaline-earth element.

147. (Added) The superconductive method according to claim 146 in

which the rare-earth or rare-earth-like element is lanthanum.

148. (added) The superconductive method according to claim 146 in which the alkaline-earth element is barium.

149. (Added) The superconductive method according to claim 145 in which the copper-oxide compound of the superconductive composition includes mixed valent copper ions.

150. (Added) The superconductive method according to claim 149 in which the copper-oxide compound includes at least one element in a nonstoichiometric atomic proportion.

151. (Added) The superconductive method according to claim 150 in which oxygen is present in the copper-oxide compound in a nonstoichiometric atomic proportion.

152. (Added) A superconductive method for conducting an electric current essentially without resistive losses, comprising:  
(a) providing a superconductor element made of a superconductive composition, the superconductive composition



consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a rare-earth element and a Group III B element and at least one alkaline-earth element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26 K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

153. (Added) The superconductive method according to claim 103 in which said at least one element is lanthanum.

154. (Added) The superconductive method according to claim 152 in

which the alkaline-earth element is barium.

155. (Added) The superconductive method according to claim 152 in which the copper-oxide compound of the superconductive composition includes mixed valent copper ions.

156. (Added) The superconductive method according to claim 155 in which the copper-oxide compound includes at least one element in a nonstoichiometric atomic proportion.

157. (Added) The superconductive method according to claim 156 in which oxygen is present in the copper-oxide compound in a nonstoichiometric atomic proportion.

158. (Added) A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive

composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element, a rare earth element; and a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

159. (Added) A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the copper-oxide

compound including at least one element selected from the group consisting of a Group II A element, a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

160. (Added) A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite

crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

161. (Added) A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting

of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive-resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

162. (Added) A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal oxide compound having a substantially layered perovskite crystal structure, the composition having a superconductive

transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

163. (Added) A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal-oxide compound having a substantially layered perovskite crystal structure, the transition metal-oxide compound including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and

a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

### **REMARKS**

Reconsideration is respectfully requested in view of and changes to the claims and the remarks herein. Please contact the undersigned to conduct a telephone interview in accordance with MPEP 713.01 to resolve any remaining requirements and/or issues prior to sending another Office Action. Relevant portions of MPEP 713.01 are included on the signature page of this amendment. In view of the changes to the claims and the remarks herein, the Examiner is respectfully requested to reconsider the above-identified application. If the



Examiner wishes to discuss the application further, or if additional information would be required, the undersigned will cooperate fully to assist in the prosecution of this application.

In paragraphs 6-7 on pages 12 -16 of the referenced office action Claims 86-87, 96-108, 115, 118, 120, 122, 123, 129-135 and 137-142 have been rejected under 35 USC 112.

The Advisory action dated Feb. 25, 1999 states that applicants response to the final rejection filed 12/14/198 ... will not be entered." In the note the examiner states "[n]ewly added 143 -177 do not simplify or reduce issues for appeal." Claims 143-163 added by this amendment correspond to in claims 86-87, 96-108, 112, 113, 117, 118, 122, and 123. Claims 143-163 added by this amendment have the same wording as claims 86-87, 96-108, 112, 113, 117, 118, 122, and 123 and include all changes suggested by the examiner to overcome the rejections of claims 86-87, 96-108, 112, 113, 117, 118, 122, and 123 claims under 35 USC 112, second paragraph.

Applicants had a telephone discussion with Examiner Kopec prior to submitting applicants' response filed on 12/14/198 in response to the final rejection. Applicants explained to Examiner Kopec that they intended to add claims (claims 143-163 ) that would not add any new issues, would reduce the number of issues under 35 USC 112 in regards to these added claims and would not cause a withdrawal of the final rejection. Examiner Kopec agreed with these comments and preliminarily agreed to enter the amendment filed 12/14/198 containing added claims 143-163. As indicated above that amendment was not entered. The present amendment adds claims 143-163 separately. Applicants request entry of the present amendment for the reasons given above.

In a separate amendment, claims 115-142 have been amended to include all suggestions of the examiner to over come the rejections under 35 USC 112,

second paragraph, except for those directed to the terms "layer-like", "perovskite-like", "rare-earth-like", and "layer-type". These terms occur in claims 86-87, 96-108, 112, 113, 117, 118, 122, and 123. The examiner agreed to enter the amendment to claims 115 - 142 if submitted separately. As stated by applicants in previous responses the terms "layer-like", "perovskite-like", "rare-earth-like", and "layer-type" are terms of art and well understood by persons of skill in the art.

In paragraph 5 of the referenced office action claims 129-131, 134, 135, 139-142 added by applicants in there response dated April 27, 1998 have been rejected under 35 USC 112 as not enabled. Applicants respectfully disagree. The examiner has given no specific reason why these claims are not enabled.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

If the above-identified Examiner's Action is a final Action, and if the above-identified application will be abandoned without further action by applicants, applicants file a Notice of Appeal to the Board of Appeals and Interferences appealing the final rejection of the claims in the above-identified Examiner's Action. Please charge deposit account 09-0468 any fee necessary to enter such Notice of Appeal.

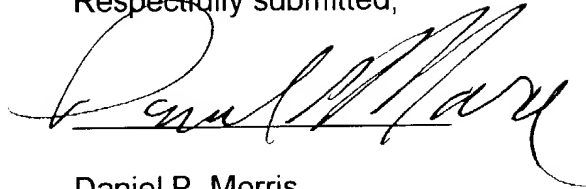
In the event that this amendment does not result in allowance of all such claims, the undersigned attorney respectfully requests a telephone interview at the Examiner's earliest convenience.

MPEP 713.01 states in part as follows:

Where the response to a first complete action includes a request for an interview or a telephone consultation to be initiated by the

examiner, ... the examiner, as soon as he or she has considered the effect of the response, should grant such request if it appears that the interview or consultation would result in expediting the case to a final action.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Daniel P. Morris", written over a horizontal line.

Daniel P. Morris  
Reg. No. 32,053  
(914) 945-3217

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598

00-IBM YORKTOWN

	DATE	TIME	TO/FROM	MODE	MIN/SEC	PGS	CMD#	STATUS
16	06/15	10:36	7033057718	EC--S	01'14"	006	243	OK

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: June 15, 1999

Serial No. 08/303,561

Group Art Unit: 1105

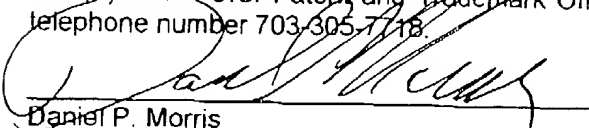
Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

**CERTIFICATE OF FACSIMILE TRANSMISSION**

I hereby certify that this paper is being facsimile transmitted under Rule CFR 1.61(d) to the U.S. Patent and Trademark Office on the date shown above To telephone number 703-305-7718.

  
Daniel P. Morris  
Reg. No. 32,053

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**Amendment After Final Rejection**

In response to the final rejection dated June 25, 1998 please consider the following:

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: June 15, 1999

Serial No. 08/303,561

Group Art Unit: 1105

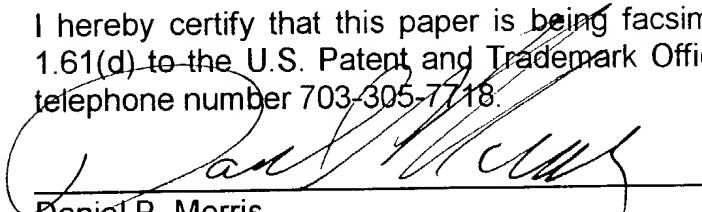
Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

**CERTIFICATE OF FACSIMILE TRANSMISSION**

I hereby certify that this paper is being facsimile transmitted under Rule CFR 1.61(d) to the U.S. Patent and Trademark Office on the date shown above To telephone number 703-305-7718.

  
\_\_\_\_\_  
Daniel P. Morris  
Reg. No. 32,053

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**Amendment After Final Rejection**

In response to the final rejection dated June 25, 1998 please consider the  
following:

## IN THE CLAIMS

164. (Added) A method according to claim 129 wherein said composition comprises a substantially layered perovskite crystal structure.
165. (Added) A method according to claim 130 wherein said superconducting transistor metal oxide comprises a substantially layered perovskite crystal structure.
166. (Added) A method according to claim 131 wherein said superconducting copper oxide comprises a substantially layered perovskite crystal structure.
167. (Added) A method according to claim 132 wherein said superconducting oxide composition comprises a substantially layered perovskite crystal structure.
168. (Added) A method according to claim 133 wherein said superconducting oxide composition comprises a substantially layered perovskite crystal structure.

169. (Added) A method according to claim 134 wherein said transistor metal oxide comprises a substantially layered perovskite crystal structure.

170. (Added) A method according to claim 135 wherein said copper oxide comprises a substantially layered perovskite crystal structure.

171. (Added) A method according to claim 136 wherein said composition comprises a substantially layered perovskite crystal structure.

172. (Added) A method according to claim 137 wherein said composition of matter comprises a substantially layered perovskite crystal structure.

173. (Added) A method according to claim 138 wherein said composition of matter comprises substantially layered perovskite crystal structure.

174. (Added) A method according to claim 139 wherein said composition of matter comprises a substantially layered perovskite crystal structure.

175. (Added) A method according to claim 140 wherein said composition of matter comprises substantially layered perovskite crystal structure.

176. (Added) A method according to claim 141 wherein said transistion metal oxide comprises substantially layered perovskite crystal structure.

177. (Added) A method according to claim 142 wherein said copper oxide composition comprises substantially layered perovskite crystal structure.

### **REMARKS**

Reconsideration is respectfully requested in view of and changes to the claims and the remarks herein. Please contact the undersigned to conduct a telephone interview in accordance with MPEP 713.01 to resolve any remaining requirements and/or issues prior to sending another Office Action. Relevant portions of MPEP 713.01 are included on the signature page of this amendment. In view of the changes to the claims and the remarks herein, the Examiner is respectfully requested to reconsider the above-identified application. If the Examiner wishes to discuss the application further, or if additional information would be required, the undersigned will cooperate fully to assist in the prosecution of this application.

The Advisory action dated Feb. 25, 1999 states that applicants response to the final rejection filed 12/14/198 ... will not be entered." In the note the examiner states "[n]ewly added 143 -177 do not simplify or reduce issues for appeal." The present separately adds claims 164-177.

Support for added claims 164-177 is found throughout the specification and claims. Each of these claims depend from another claim and add the limitation



"comprises substantially layered perovskite crystal structure". Applicants are adding these dependent claims since the examiner at page 11 paragraph (1) of the final action dated May 27, 1997 suggested using this language. Entry of claims 164 - - 177 does not require withdrawal of the finality of the rejection.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

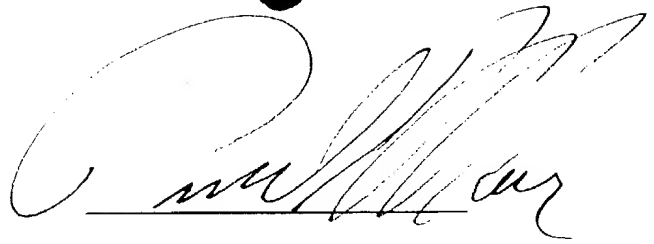
If the above-identified Examiner's Action is a final Action, and if the above-identified application will be abandoned without further action by applicants, applicants file a Notice of Appeal to the Board of Appeals and Interferences appealing the final rejection of the claims in the above-identified Examiner's Action. Please charge deposit account 09-0468 any fee necessary to enter such Notice of Appeal.

In the event that this amendment does not result in allowance of all such claims, the undersigned attorney respectfully requests a telephone interview at the Examiner's earliest convenience.

MPEP 713.01 states in part as follows:

Where the response to a first complete action includes a request for an interview or a telephone consultation to be initiated by the examiner, ... the examiner, as soon as he or she has considered the effect of the response, should grant such request if it appears that the interview or consultation would result in expediting the case to a final action.

Respectfully submitted,

A handwritten signature in black ink, appearing to read 'Daniel P. Morris', is written over a horizontal line.

Daniel P. Morris  
Reg. No. 32,053  
(914) 945-3217

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598

	DATE	TIME	TO/FROM	MODE	MIN/SEC	PGS	CMD#	STATUS
15	06/14	15:53	7033057718	EC--S	02'04"	010	241	OK

---

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: June 14, 1999

Serial No. 08/303,561

Group Art Unit: 1105

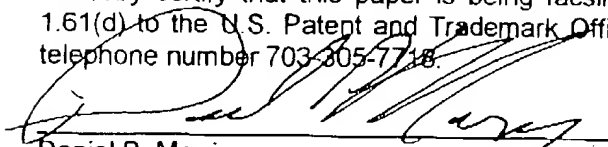
Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

**CERTIFICATE OF FACSIMILE TRANSMISSION**

I hereby certify that this paper is being facsimile transmitted under Rule CFR 1.61(d) to the U.S. Patent and Trademark Office on the date shown above To telephone number 703-305-7718.



Daniel P. Morris  
Reg. No. 32,053

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**Amendment After Final Rejection**

In response to the final rejection dated June 25, 1998 please consider the following:

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: June 14, 1999

Serial No. 08/303,561

Group Art Unit: 1105

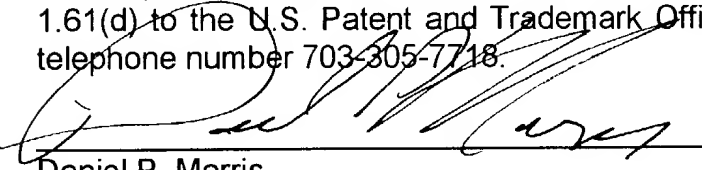
Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

**CERTIFICATE OF FACSIMILE TRANSMISSION**

I hereby certify that this paper is being facsimile transmitted under Rule CFR 1.61(d) to the U.S. Patent and Trademark Office on the date shown above To telephone number 703-305-7718.

  
Daniel P. Morris  
Reg. No. 32,053

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**Amendment After Final Rejection**

In response to the final rejection dated June 25, 1998 please consider the  
following:

## IN THE CLAIMS

115. (Amended) A method comprising the steps of:

forming a composition including copper, oxygen and [any] an  
element selected from the group consisting of at least one  
Group II A element and at least one element selected from

the group consisting of a rare earth element and a Group  
III B element, where said composition is a mixed copper

oxide having a non-stoichiometric amount of oxygen therein  
and exhibiting a superconducting state at a temperature greater  
than 26°K;

maintaining said composition in said superconducting state at a  
temperature greater than 26°K; and

passing an electrical current through said composition while  
said composition is in said superconducting state.

120. (Amended) A method comprising the steps of:

forming a composition including a transition metal, oxygen and [any] an element selected from the group consisting of at least one Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, where said composition is a mixed transitional metal oxide formed from said transition metal and said oxygen, said mixed transition metal oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K;

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

123. (Amended) A superconductive method for conducting an electric current

essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting

essentially of a transition metal-oxide compound having a layer-type perovskite-like crystal structure, the transition metal-oxide compound including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $[T] T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor

element.

129. (Amended) A method comprising providing a composition having a transition temperature greater than 26°K, the composition including a rare earth or alkaline earth element, a transition metal element capable of exhibiting multivalent states and oxygen, including at least one phase that exhibits superconductivity at temperature in excess of 26°K, maintaining said composition at said temperature to exhibit said superconductivity and passing an electrical superconducting current through said composition [while] with said phase exhibiting said superconductivity.

130. (Amended). A method comprising providing a superconducting transition metal oxide having a superconductive onset temperature greater than 26°K, maintaining said superconducting transition metal oxide [being] at a temperature less than said superconducting onset temperature and flowing a superconducting current therein.

131. (Amended). A method comprising providing a superconducting copper



oxide having a superconductive onset temperature greater than 26°K, [maintaing] maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a superconducting current [therein] in said superconducting oxide.

132. (Amended) . A method comprising providing a superconducting oxide composition having a superconductive onset temperature greater than 26°K, maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a [superconducting] superconducting current therein, said composition comprising at least one each of rare earth, an alkaline earth, and copper.

133. (Amended). A method comprising providing a superconducting oxide composition having a superconductive onset temperature greater than 26°K, [maintianing] maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a superconducting electrical current therein, said composition comprising at least one each of a Group III B element, an alkaline earth, and copper.

134. (Amended) A method comprising flowing a superconducting electrical current in a transition metal oxide having a  $T_c$  greater than 26°K and

maintianing said transition metal oxide at a temperature less than said  $T_c$ .

135. (Amended) A method comprising flowing a superconducting electrical current in a copper oxide having a  $T_c$  greater than 26°K and maintianing said copper oxide at a temperature less than said  $T_c$ .

137. (Amended) A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  greater than 26°K, said composition comprising at least one each of a III B element, an alkaline earth, and copper oxide and maintianing said composition of matter at a temperature less than said  $T_c$ .

138. (Amended) A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  greater than 26°K, said composition comprising at least one each of a rare earth, alkaline earth, and copper oxide and maintianing said composition of matter at a temperature less than said  $T_c$ .

139. (Amended) A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  greater than 26°K, said composition comprising at least one each of a rare

earth, and copper oxide and maintaining said composition of matter at a temperature less than said  $T_c$ .

140. (Amended) A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  greater than 26°K carrying, said composition comprising at least one each of a III B element, and copper oxide and maintaining said composition of matter at a temperature less than said  $T_c$ .

141. (Amended) A method comprising flowing a superconducting electrical current in a transition metal oxide comprising a  $T_c > 26^\circ\text{K}$  and maintaining said transition metal oxide at a temperature less than said  $T_c$ .

142. (Amended) A method comprising flowing a superconducting electrical current in a copper oxide composition of matter comprising a  $T_c > 26^\circ\text{K}$  and maintaining said copper oxide composition of matter at a temperature less than said [TC]  $T_c$ .

Added claims:

#### **REMARKS**

Reconsideration is respectfully requested in view of and changes to the claims and the remarks herein. Please contact the undersigned to conduct a telephone interview in accordance with MPEP 713.01 to resolve any remaining requirements and/or issues prior to sending another Office Action. Relevant portions of MPEP 713.01 are included on the signature page of this amendment. In view of the changes to the claims and the remarks herein, the Examiner is respectfully requested to reconsider the above-identified application. If the Examiner wishes to discuss the application further, or if additional information would be required, the undersigned will cooperate fully to assist in the prosecution of this application.

The Advisory action dated Feb. 25, 1999 states that applicants response to the final rejection filed 12/14/198 ... will not be entered." In the note the examiner states "[t]he amendments to claims 115 - 142 will be entered if submitted separately." This amendment is a separate submission of the amendments to claims 115 - 142.

In paragraphs 6-7 on pages 12 -16 of the referenced office action Claims 86-87, 96-108, 115, 118, 120, 122, 123, 129-135 and 137-142 have been rejected under 35 USC 112. All changes suggested by the examiner have been made except for those directed to the terms "layer-like", "perovskite-like", "rare-earth-like", and "layer-type". These terms occur in claims 86-87, 96-108, 112, 113, 117, 118, 122, and 123. As stated by applicants in previous responses these are terms of art and well understood by persons of skill in the art.

In paragraph 5 of the referenced office action claims 129-131, 134, 135, 139-142 added by applicants in there response dated April 27, 1998 have been rejected under 35 USC 112 as not enabled. Applicants respectfully disagree. The examiner has given no specific reason why these claims are not enabled.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

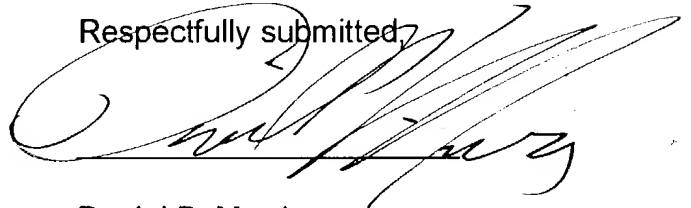
If the above-identified Examiner's Action is a final Action, and if the above-identified application will be abandoned without further action by applicants, applicants file a Notice of Appeal to the Board of Appeals and Interferences appealing the final rejection of the claims in the above-identified Examiner's Action. Please charge deposit account 09-0468 any fee necessary to enter such Notice of Appeal.

In the event that this amendment does not result in allowance of all such claims, the undersigned attorney respectfully requests a telephone interview at the Examiner's earliest convenience.

MPEP 713.01 states in part as follows:

Where the response to a first complete action includes a request for an interview or a telephone consultation to be initiated by the examiner, ... the examiner, as soon as he or she has considered the effect of the response, should grant such request if it appears that the interview or consultation would result in expediting the case to a final action.

Respectfully submitted,

A handwritten signature in black ink, appearing to read 'Daniel P. Morris', written over a horizontal line.

Daniel P. Morris  
Reg. No. 32,053  
(914) 945-3217

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598



## Patent and Trademark Office

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.
08/303,561	09/09/94	REPUBLIC	J YUS87074RY

DANIEL P MORRIS  
IBM CORPORATION  
INTELLECTUAL PROPERTY LAW DEPARTMENT  
P O BOX 218  
YORKTOWN HEIGHTS NY 10598

105/10225

EXAMINER	
KOPECKI	
ART UNIT	PAPER NUMBER
1751	77A

DATE MAILED: 02/25/99

Below is a communication from the EXAMINER in charge of this application  
COMMISSIONER OF PATENTS AND TRADEMARKS

## ADVISORY ACTION

☒ THE PERIOD FOR RESPONSE:

- ☒ is extended to run 6 mos. from the date of the Final Rejection
- ☐ continues to run \_\_\_\_\_ from the date of the Final Rejection
- ☐ expires three months from the date of the final rejection or as of the mailing date of this Advisory Action, whichever is later. In no event however, will the statutory period for response expire later than six months from the date of the final rejection.

Any extension of time must be obtained by filing a petition under 37 CFR 1.136(a), the proposed response and the appropriate fee. The date on which the response, the petition, and the fee have been filed is the date of the response and also the date for the purposes of determining the period of extension and the corresponding amount of the fee. Any extension fee pursuant to 37 CFR 1.17 will be calculated from the date that the shortened statutory period for response expires as set forth above.

☐ Appellant's Brief is due in accordance with 37 CFR 1.192(a).☒ Applicant's response to the final rejection, filed 12/10/98, has been considered with the following affect, but it is not deemed to place the application in condition for allowance: 12/23/98

1. ☐ The proposed amendments to the claim and/or specification will not be entered and the final rejection stands because:
- ☐ There is no convincing showing under 37 CFR 1.116(b) why the proposed amendment is necessary and was not earlier presented.
  - ☐ They raise new issues that would require further consideration and/or search. (See Note).
  - ☐ They raise the issue of new matter. (See Note).
  - ☐ They are not deemed to place the application in better form for appeal by materially reducing or simplifying the issues for appeal.
  - ☐ They present additional claims without cancelling a corresponding number of finally rejected claims.

NOTE: The terminology "lyot-type" or "perovskite-like" has been rejected under 35 USC 112, 2nd P. since it is not the REJECTION written 8/26/92. The newly filed exhibits are considered untimely.

2. ☐ Newly proposed or amended claims non-allowable claims. would be allowed if submitted in a separately filed amendment cancelling the
3. ☐ Upon the filing of an appeal, the proposed amendment ☐ will be ☐ will not be, entered and the status of the claims in this application would be as follows:
- Allowed claims: \_\_\_\_\_
- Claims objected to: \_\_\_\_\_
- Claims rejected: \_\_\_\_\_
- However:
- ☐ The rejection of claims \_\_\_\_\_ on references is deemed to be overcome by applicant's response.
  - ☐ The rejection of claims \_\_\_\_\_ on non-reference grounds only is deemed to be overcome by applicant's response.
4. ☐ The affidavit, exhibit or request for reconsideration has been considered but does not overcome the rejection.
5. ☒ The affidavit or exhibit will not be considered because applicant has not shown good and sufficient reasons why it was not earlier presented. SEE NOTE
- ☐ The proposed drawing correction ☐ has ☐ has not been approved by the examiner.
- ☐ Other

*Mark Kopec*  
Mark Kopec  
Primary Examiner



## Patent and Trademark Office

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.
08/300,561	09/09/94	IBM CORP.	00447484

DANIEL P. MURKIS  
IBM CORPORATION  
INTELLECTUAL PROPERTY LAW DEPARTMENT  
P O BOX 218  
YORKTOWN HEIGHTS NY 10598

EXAMINER	
KOPEC, M	
ART UNIT	PAPER NUMBER
1/51	778

DATE MAILED: 01/25/99

Below is a communication from the EXAMINER in charge of this application  
COMMISSIONER OF PATENTS AND TRADEMARKS

## ADVISORY ACTION

☒ THE PERIOD FOR RESPONSE:

- ☒ is extended to run 6 mos. from the date of the Final Rejection
- ☐ continues to run \_\_\_\_\_ from the date of the Final Rejection
- ☐ expires three months from the date of the final rejection or as of the mailing date of this Advisory Action, whichever is later. In no event however, will the statutory period for response expire later than six months from the date of the final rejection.

Any extension of time must be obtained by filing a petition under 37 CFR 1.136(a), the proposed response and the appropriate fee. The date on which the response, the petition, and the fee have been filed is the date of the response and also the date for the purposes of determining the period of extension and the corresponding amount of the fee. Any extension fee pursuant to 37 CFR 1.17 will be calculated from the date that the shortened statutory period for response expires as set forth above.

☒ Appellant's Brief is due in accordance with 37 CFR 1.192(a).☒ Applicant's response to the final rejection, filed 12/15/98, has been considered with the following affect, but it is not deemed to place the application in condition for allowance:

1. ☐ The proposed amendments to the claim and/or specification will not be entered and the final rejection stands because:
- ☐ There is no convincing showing under 37 CFR 1.116(b) why the proposed amendment is necessary and was not earlier presented.
  - ☐ They raise new issues that would require further consideration and/or search. (See Note).
  - ☐ They raise the issue of new matter. (See Note).
  - ☐ They are not deemed to place the application in better form for appeal by materially reducing or simplifying the issues for appeal.
  - ☐ They present additional claims without cancelling a corresponding number of finally rejected claims.

NOTE: The 112, 1st P. rejections directed to enablement, to which the newly submitted affidavit pertains, have been of record since at least 8/26/92. The newly filed affidavit is considered untimely.

2. ☐ Newly proposed or amended claims \_\_\_\_\_ would be allowed if submitted in a separately filed amendment cancelling the non-allowable claims.
3. ☐ Upon the filing of an appeal, the proposed amendment ☐ will be ☐ will not be, entered and the status of the claims in this application would be as follows:
- Allowed claims: \_\_\_\_\_
- Claims objected to: \_\_\_\_\_
- Claims rejected: \_\_\_\_\_
- However;
- ☐ The rejection of claims \_\_\_\_\_ on references is deemed to be overcome by applicant's response.
  - ☐ The rejection of claims \_\_\_\_\_ on non-reference grounds only is deemed to be overcome by applicant's response.
4. ☐ The affidavit, exhibit or request for reconsideration has been considered but does not overcome the rejection.
5. ☒ The affidavit or exhibit will not be considered because applicant has not shown good and sufficient reasons why it was not earlier presented. SEE NOTE
- ☐ The proposed drawing correction ☐ has ☐ has not been approved by the examiner.
- ☐ Other

*Mark Kopec*  
Mark Kopec  
Primary Examiner

DEPARTMENT OF COMMERCE  
DANIEL F. ROBERTS  
IBM CORPORATION



Patent and Trademark Office

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.
P.O. BOX 210		YORKTOWN HEIGHTS NY 10593	117257-01

EXAMINER	
ART UNIT	PAPER NUMBER
	77C

DATE MAILED:

Below is a communication from the EXAMINER in charge of this application  
COMMISSIONER OF PATENTS AND TRADEMARKS

### ADVISORY ACTION

☒ THE PERIOD FOR RESPONSE:

- ☒ is extended to run 6 mos from the date of the Final Rejection
- ☐ continues to run \_\_\_\_\_ from the date of the Final Rejection
- ☐ expires three months from the date of the final rejection or as of the mailing date of this Advisory Action, whichever is later. In no event however, will the statutory period for response expire later than six months from the date of the final rejection.

Any extension of time must be obtained by filing a petition under 37 CFR 1.136(a), the proposed response and the appropriate fee. The date on which the response, the petition, and the fee have been filed is the date of the response and also the date for the purposes of determining the period of extension and the corresponding amount of the fee. Any extension fee pursuant to 37 CFR 1.17 will be calculated from the date that the shortened statutory period for response expires as set forth above.

☒ Appellant's Brief is due in accordance with 37 CFR 1.192(a).

☒ Applicant's response to the final rejection, filed 12/14/98 has been considered with the following affect, but it is not deemed to place the application in condition for allowance:

1. ☒ The proposed amendments to the claim and/or specification will not be entered and the final rejection stands because:
- ☐ There is no convincing showing under 37 CFR 1.116(b) why the proposed amendment is necessary and was not earlier presented.
  - ☐ They raise new issues that would require further consideration and/or search. (See Note).
  - ☐ They raise the issue of new matter. (See Note).
  - ☒ They are not deemed to place the application in better form for appeal by materially reducing or simplifying the issues for appeal.
  - ☒ They present additional claims without cancelling a corresponding number of finally rejected claims.

NOTE: Newly added claims 143-147 do not simplify or reduce issues for appeal. The amendments to claims 115-142, which overcome several 112, 2nd TP rejections of record, will be entered if submitted separately.

2. ☐ Newly proposed or amended claims \_\_\_\_\_ would be allowed if submitted in a separately filed amendment cancelling the non-allowable claims.
3. ☒ Upon the filing of an appeal, the proposed amendment ☐ will be ☒ will not be, entered and the status of the claims in this application would be as follows:
- Allowed claims: 136
- Claims objected to: \_\_\_\_\_
- Claims rejected: 24-26, 86-90, 111-135, 137-142
- However:
- ☐ The rejection of claims \_\_\_\_\_ on references is deemed to be overcome by applicant's response.
  - ☐ The rejection of claims \_\_\_\_\_ on non-reference grounds only is deemed to be overcome by applicant's response.
4. ☐ The affidavit, exhibit or request for reconsideration has been considered but does not overcome the rejection.
5. ☐ The affidavit or exhibit will not be considered because applicant has not shown good and sufficient reasons why it was not earlier presented.
- ☐ The proposed drawing correction ☐ has ☐ has not been approved by the examiner.
- ☐ Other: \_\_\_\_\_

*Mark Kopec*  
Mark Kopec  
Primary Examiner





Patent and Trademark Office

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.
08/303,561	09/09/94	IBM CORPORATION	1000707931

DANIEL F. BURKIS  
IBM CORPORATION  
INTELLECTUAL PROPERTY LAW DEPARTMENT  
P O BOX 218  
YORKTOWN HEIGHTS NY 10598

1001707931

EXAMINER	
ROBERT N.	
ART UNIT	PAPER NUMBER
1/51	770

DATE MAILED: 02/25/95

Below is a communication from the EXAMINER in charge of this application  
COMMISSIONER OF PATENTS AND TRADEMARKS

ADVISORY ACTION

☒ THE PERIOD FOR RESPONSE:

- ☒ is extended to run 6 mos from the date of the Final Rejection
- ☐ continues to run \_\_\_\_\_ from the date of the Final Rejection
- ☐ expires three months from the date of the final rejection or as of the mailing date of this Advisory Action, whichever is later. In no event however, will the statutory period for response expire later than six months from the date of the final rejection.

Any extension of time must be obtained by filing a petition under 37 CFR 1.136(a), the proposed response and the appropriate fee. The date on which the response, the petition, and the fee have been filed is the date of the response and also the date for the purposes of determining the period of extension and the corresponding amount of the fee. Any extension fee pursuant to 37 CFR 1.17 will be calculated from the date that the shortened statutory period for response expires as set forth above.

- ☒ Appellant's Brief is due in accordance with 37 CFR 1.192(a).
- ☒ Applicant's response to the final rejection, filed 12/24/98, has been considered with the following affect, but it is not deemed to place the application in condition for allowance:

27

1. ☐ The proposed amendments to the claim and/or specification will not be entered and the final rejection stands because:
- ☐ There is no convincing showing under 37 CFR 1.116(b) why the proposed amendment is necessary and was not earlier presented.
  - ☐ They raise new issues that would require further consideration and/or search. (See Note).
  - ☐ They raise the issue of new matter. (See Note).
  - ☐ They are not deemed to place the application in better form for appeal by materially reducing or simplifying the issues for appeal.
  - ☐ They present additional claims without cancelling a corresponding number of finally rejected claims.

NOTE: The terminology "comprising" and "including" have been rejected under 35 USC 112, 2nd ID. since it limit the REJECTION mailed 8/26/92. The newly filed exhibits are considered untimely.

2. ☐ Newly proposed or amended claims non-allowable claims. would be allowed if submitted in a separately filed amendment cancelling the
3. ☐ Upon the filing of an appeal, the proposed amendment ☐ will be ☐ will not be, entered and the status of the claims in this application would be as follows:
- Allowed claims: \_\_\_\_\_
- Claims objected to: \_\_\_\_\_
- Claims rejected: \_\_\_\_\_
- However:
- ☐ The rejection of claims \_\_\_\_\_ on references is deemed to be overcome by applicant's response.
  - ☐ The rejection of claims \_\_\_\_\_ on non-reference grounds only is deemed to be overcome by applicant's response.
4. ☐ The affidavit, exhibit or request for reconsideration has been considered but does not overcome the rejection.
5. ☒ The affidavit or exhibit will not be considered because applicant has not shown good and sufficient reasons why it was not earlier presented. SEE NOTE
- ☐ The proposed drawing correction ☐ has ☐ has not been approved by the examiner.
- ☐ Other

*Mark Kopec*  
Mark Kopec  
Primary Examiner



Patent and Trademark Office

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.
0873003-563	09/09/94	IBM CORP	1

DANIEL F. MORRIS  
IBM CORPORATION  
INTELLECTUAL PROPERTY LAW DEPARTMENT  
P.O. BOX 218  
YORKTOWN HEIGHTS, NY 10598

EXAMINER	
BUTLER	
ART UNIT	PAPER NUMBER
1751	77E

DATE MAILED: 02/25/95

Below is a communication from the EXAMINER in charge of this application  
COMMISSIONER OF PATENTS AND TRADEMARKS

ADVISORY ACTION

☒ THE PERIOD FOR RESPONSE:

- ☒ is extended to run 6 mos. from the date of the Final Rejection
- ☐ continues to run \_\_\_\_\_ from the date of the Final Rejection
- ☐ expires three months from the date of the final rejection or as of the mailing date of this Advisory Action, whichever is later. In no event however, will the statutory period for response expire later than six months from the date of the final rejection.

Any extension of time must be obtained by filing a petition under 37 CFR 1.136(a), the proposed response and the appropriate fee. The date on which the response, the petition, and the fee have been filed is the date of the response and also the date for the purposes of determining the period of extension and the corresponding amount of the fee. Any extension fee pursuant to 37 CFR 1.17 will be calculated from the date that the shortened statutory period for response expires as set forth above.

☒ Appellant's Brief is due in accordance with 37 CFR 1.192(a).

☒ Applicant's response to the final rejection, filed 12/16/98, has been considered with the following affect, but it is not deemed to place the application in condition for allowance: 12/24/98

1. ☐ The proposed amendments to the claim and/or specification will not be entered and the final rejection stands because:
- ☐ There is no convincing showing under 37 CFR 1.116(b) why the proposed amendment is necessary and was not earlier presented.
  - ☐ They raise new issues that would require further consideration and/or search. (See Note).
  - ☐ They raise the issue of new matter. (See Note).
  - ☐ They are not deemed to place the application in better form for appeal by materially reducing or simplifying the issues for appeal.
  - ☐ They present additional claims without cancelling a corresponding number of finally rejected claims.

NOTE: \_\_\_\_\_

2. ☐ Newly proposed or amended claims \_\_\_\_\_ would be allowed if submitted in a separately filed amendment cancelling the non-allowable claims.

3. ☐ Upon the filing of an appeal, the proposed amendment ☐ will be ☐ will not be, entered and the status of the claims in this application would be as follows:

Allowed claims: \_\_\_\_\_

Claims objected to: \_\_\_\_\_

Claims rejected: \_\_\_\_\_

However;

- ☐ The rejection of claims \_\_\_\_\_ on references is deemed to be overcome by applicant's response.
  - ☐ The rejection of claims \_\_\_\_\_ on non-reference grounds only is deemed to be overcome by applicant's response.
4. ☒ The affidavit, exhibit or request for reconsideration has been considered but does not overcome the rejection. SEE ATTACH
5. ☐ The affidavit or exhibit will not be considered because applicant has not shown good and sufficient reasons why it was not earlier presented.

- ☐ The proposed drawing correction ☐ has ☐ has not been approved by the examiner.

☐ Other

*Mark Kopec*

Mark Kopec  
Primary Examiner

Art Unit: 1751

The additional 1.132 Affidavits of Mitzi, Tsuei and Dinger (filed 12/16/98) and the newly provided 1.132 Affidavits of Thomas Shaw (filed 12/16/98) and Peter Duncombe (filed 12/21/98) have been reviewed and considered.

The examiner notes the books describing the general principles of ceramic fabrication provided in these Affidavits. Also, the examiner notes that such fabrication techniques were utilized subsequently (after the filing date of the instant application) to produce the superconductive materials described in the Poole et al reference as well as the materials produced by Peter Duncombe (see Affidavit filed 12/21/98).

It is the examiner's maintained position that while general principles of ceramic fabrication were most certainly known prior to the filing date of the instant application, the utilization of such techniques to produce superconductive materials within the scope of the instant claims were not known. The affidavits are not effective to demonstrate enablement *at the time* the invention was made. As stated in paper #66, page 8, one may now know of a material that superconducts at more than 26K, but the affidavits do not establish the existence of that knowledge on the filing date of the present application.

Art Unit: 1751

It is acknowledged that applicants are pioneers in the filed of high temperature metal oxide superconductivity. The examiner respectfully maintains, for the reasons of record, that the disclosure is not fully enabling for the scope of the present claims.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Mark Kopec whose telephone number is (703) 308-1088. The examiner can normally be reached on Monday-Thursday from 7:30 AM - 6:00 PM.

If reasonable attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Dr. Yogendra Gupta, can be reached on (703) 308-4708. The fax phone number for this Group is (703) 305-3599.

Any inquiry of a general nature or relating to the status of this application should be directed to the Group receptionist whose telephone number is (703) 308-0661.

  
Mark Kopec  
Primary Examiner

Mark Kopec  
February 22, 1999



UNITED STATES DEPARTMENT OF COMMERCE  
Patent and Trademark Office  
Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

APPLICATION NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.
--------------------	-------------	-----------------------	---------------------

EXAMINER
----------

ART UNIT	PAPER NUMBER
----------	--------------

DATE MAILED:

### INTERVIEW SUMMARY

All participants (applicant, applicant's representative, PTO personnel):

(1) Daniel P. Morris (3) \_\_\_\_\_  
(2) Mark Kopeck (4) \_\_\_\_\_

Date of Interview 2/18/99

Type: ☒ Telephonic ☐ Personal (copy is given to ☐ applicant ☐ applicant's representative).

Exhibit shown or demonstration conducted: ☐ Yes ☒ No If yes, brief description: \_\_\_\_\_

Agreement ☐ was reached. ☐ was not reached.

Claim(s) discussed: \_\_\_\_\_

Identification of prior art discussed: \_\_\_\_\_

Description of the general nature of what was agreed to if an agreement was reached, or any other comments: Examiner  
requested a copy of the 1,132 affidavit of Thomas M. Shaw  
(remarks filed 12/16/98).

(A fuller description, if necessary, and a copy of the amendments, if available, which the examiner agreed would render the claims allowable must be attached. Also, where no copy of the amendments which would render the claims allowable is available, a summary thereof must be attached.)

1. ☒ It is not necessary for applicant to provide a separate record of the substance of the interview.

Unless the paragraph above has been checked to indicate to the contrary. A FORMAL WRITTEN RESPONSE TO THE LAST OFFICE ACTION IS NOT WAIVED AND MUST INCLUDE THE SUBSTANCE OF THE INTERVIEW. (See MPEP Section 713.04). If a response to the last Office action has been ready been filed, APPLICANT IS GIVEN ONE MONTH FROM THIS INTERVIEW DATE TO FILE A STATEMENT OF THE SUBSTANCE OF THE INTERVIEW.

2. ☐ Since the Examiner's interview summary above (including any attachments) reflects a complete response to each of the objections, rejections and requirements that may be present in the last Office action, and since the claims are now allowable, this completed form is considered to fulfill the response requirements of the last Office action. Applicant is not relieved from providing a separate record of the interview unless box 1 above is also checked.

Examiner Note: You must sign this form unless it is an attachment to another form.

Mark Kopeck 2/18/99



UNITED STATES DEPARTMENT OF COMMERCE  
Patent and Trademark Office  
Assistant Secretary and Commissioner of  
Patents and Trademarks  
Washington, D.C. 20231

10987-074BY  
DPM

MAILED: FEB 8 1999

Paper No. 70

In re application of

: J. Bednorz et al.

Serial Number: 08/303561

: DECISION ON PETITION

Filed: September 09, 1994

: UNDER 37 C.F.R. 1.181

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

This is a decision on the Petition for Withdrawal of the Final Rejection, filed December 3, 1998 seeking to withdraw the finality of the Office Action of June 25, 1998. This petition is appropriate under 37 CFR 1.181. The Petitioner asserts that the finality is improper and requests a new non-final action. The Petitioner states that: "Applicants are entitled to know why the examiner has maintained the rejection under 35 USC 102 and 103 over the Asahi Shinbum article in light of applicants proof which the examiner has not rebutted. Applicants are in the position of having to guess at what are the reasons for maintaining these rejections. Applicants cannot properly appeal these rejections with out knowing the examiner's reasons for maintaining the rejections."

#### BACKGROUND

Claims 24-26, 86-90, 96-135, and 137-142 have been rejected under 35 USC 102(a) as anticipated by the Asahi Shinbum article and have been rejected under 35 USC 103 as being unpatentable over the Asahi Shinbum article. According to the Petitioner, the applicants have proven (see Substitute Amendment, Paper 59, pages 22, line 8 to page 24, last line, filed March 6, 1997) that their invention was reduced to practice in the United States prior to the date of the Asahi Shinbum article. Further it is alleged that the examiner has not rebutted applicants' proof that applicants' conception was in the United States at their direction prior to the date of the Asahi Shinbum article and the examiner has not denied that applicants have proven that they were diligent by instructing coworkers in the United States from a time prior to the date of the Asahi Shinbum article until the date the examiner believes is the date of applicants' date of reduction to practice in the United States. The Petitioner takes specific issue with the examiner's response to applicants' proof (found in the above cited portion of Paper 59) at page 19, paragraph d, ii of the final rejection which concludes that: "Nevertheless, the actual reduction in this country is deemed to have occurred on December

3,1986, which is after the publication date for the reference". Again, the Petitioner urges that the final rejection should be withdrawn and requests a new non-final action containing the reason why the examiner disagrees with the applicants' proof of conception, diligence and reduction to practice in the United States prior to the date of the Asahi Shinbum article.

#### DECISION

A careful review of the application record indicates that the Petitioner's request to withdraw the finality of the June 25, 1998 office action should be denied. In the final office action mailed June 25, 1998, pages 16 through 20, the examiner has specifically and clearly addressed applicants' arguments regarding the 35 USC 102(a) rejection over the Asahi Shinbum article and proof of reduction to practice in this country as set forth in applicants Paper No. 59, filed March 6, 1997. The examiner on page 19, section d)I clearly asserts that the applicants were unable to show the attainment of superconductivity any earlier than December 3, 1986 in this country. The examiners' reason for his conclusion is: "Again, the present invention is directed to the method of superconducting electricity. That **method** (emphasis added) apparently was not reduced to practice before December 3, 1986". Thus, the final office action has in fact provided the reasons why applicants proof of an earlier reduction to practice in this country was not acceptable to the examiner. The final office action of record is considered to be proper and will not be withdrawn as Petitioner has requested.

Receipt is acknowledged for the AMENDMENT AFTER FINAL REJECTION UNDER 37 CFR 1.116 and the 37 CFR 1.132 AFFIDAVIT OF Dr. James W. Leonard filed on December 15, 1998. Both of these documents will be forwarded to the examiner of record for consideration.

The petition is **denied**.



Richard V. Fisher  
Director Group 1700  
Specialized Chemical Industries  
and Chemical Engineering

Daniel P. Morris  
IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598

00-IBM YORKTOWN

	DATE	TIME	TO/FROM	MODE	MIN/SEC	PGS	CMD#	STATUS
11	12/27	01:36	917033053599	EC--S	03'57"	018	145	OK

---

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 27, 1998

Serial No. 08/303,561

Group Art Unit: 1105

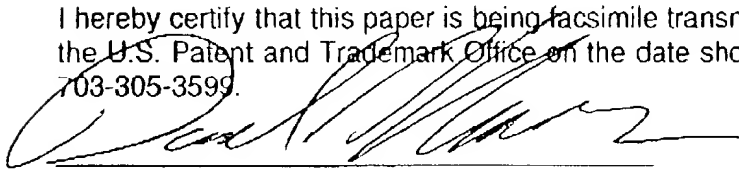
Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

I hereby certify that this paper is being facsimile transmitted under Rule CFR 1.61(d) to  
the U.S. Patent and Trademark Office on the date shown above to telephone number  
703-305-3599.



Daniel P. Morris  
Reg. No. 32,053

**AMENDMENT AFTER FINAL REJECTION UNDER 37 CFR 1.116**

Sir:

In response to the Office Action dated June 25, 1998, please consider the following:

**REMARKS**

Applicants' claims have been rejected under 35 USC 112 as indefinite for using the  
terminology "perovskite-like" and "rare-earth-like". Applicants respectfully disagree.

In addition to the evidence previously submitted showing that these are terms used by  
persons of skill in the art and that there are issued patents containing these terms in  
the claims which shows that the USPTO recognizes these terms as definite under 35



**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 27, 1998

Serial No. 08/303,561

Group Art Unit: 1105

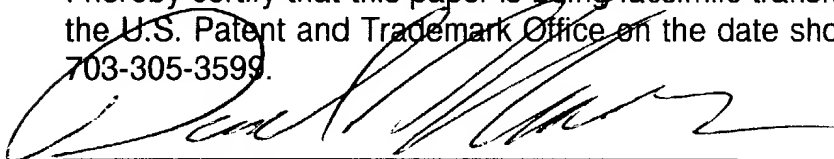
Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

I hereby certify that this paper is being facsimile transmitted under Rule CFR 1.61(d) to the U.S. Patent and Trademark Office on the date shown above to telephone number 703-305-3599.



Daniel P. Morris  
Reg. No. 32,053

**AMENDMENT AFTER FINAL REJECTION UNDER 37 CFR 1.116**

Sir:

In response to the Office Action dated June 25, 1998, please consider the following:

**REMARKS**

Applicants' claims have been rejected under 35 USC 112 as indefinite for using the terminology "perovskite-like" and "rare-earth-like". Applicants respectfully disagree.

In addition to the evidence previously submitted showing that these are terms used by persons of skill in the art and that there are issued patents containing these terms in the claims which shows that the USPTO recognizes these terms as definite under 35

USC 112, applicants submit the following additional evidence that the USPTO recognizes these terms as definite under 35 USC 112.

The undersigned attorney did a search in Lexis for the terms "like" in issued US patents. As shown in Attachment A, this search Lexis found 140,058 issued US patents using the terminology "like" in the claims. The USPTO has, therefore, accepted this terminology as definite within the meaning of 35 USC 112. A number of specific examples are provided in Attachments B to J, each of which are the results of a similar Lexis search. (Lists of the patent numbers will be provided at the request of the examiner.) Attachment B shows that there are 443 issued US patents having the term "diamond like" in the claims. Attachment C shows that there are 319 issued US patents having the term "diamond like carbon" in the claims. Attachment D shows that there are 10 issued US patents having the term "halogen like" in the claims. Attachment E shows that there are 11 issued US patents having the term "oxygen like" in the claims. Attachment F shows that there are 79 issued US patents having the term "ceramic like" in the claims. Attachment G shows that there are 31 issued US patents having the term "carbon like" in the claims. Attachment H shows that there are 5 issued US patents having the term "silicon like" in the claims. Attachment I shows that there are 10 issued US patents having the term "nitrogen like" in the claims. Attachment J shows that there are 17 issued US patents having the term "copper like" in the claims. In view thereof applicants respectfully request the examiner to withdraw the rejection of their claims as indefinite for using the terminology "perovskite like" and "rare-earth-like" since use of the term "like" is recognized as definite under 35 USC 112 by the USPTO.

Applicants claims have been rejected under 35 USC 102(a) and 103 over the Asahi Shinbum article which has a date of Nov. 28, 1986. In addition to evidence previously submitted proving that applicants conception was in the United States at applicants direction prior to Nov. 28, 1986 applicants submit the following additional evidence. Attachment K page 1 is a copy of the front cover of Zeitschrift Fur Physik B Condensed Matter Vol. 64 which contains the article ( pp 189-193) referred to and incorporated by reference at page 6, lines 6-10, of applicant's specification which applicants state is "[t]he basis or our invention". This page bears in the upper right the date stamp of the IBM Research Library bearing the date of Sept. 18, 1986. Page 2 of Attachment K is an enlarged view of the upper right corner showing the date stamp. Thus the assignee of the present invention IBM, the employer of the inventors at the time of the conception of the invention, had in its possession in the United States a copy of the article which applicants state forms the basis of their invention prior to the date of the Asahi Shinbum. Thus IBM had in its possession in the United States a written description of applicants' invention in "ready to patent form" as defined by the United States Supreme Court in Pfaff v. Wells No. 97-1130 decided November 10, 1998 prior to the date of the Asahi Shinbum article. The US Supreme Court held that "reduction to practice" is not needed to establish a date for invention. The court stated " [t]he statute's only specific reference to that term is found in §102(g), which sets fort the standard for resolving priority between two competing claimants to a patent." Since §102(g) is not applicable here, "diligence" and "reduction to practice" are not required. Applicants article in Zeitschrift Fur Physik "is proof that prior to [the date of the Asahi

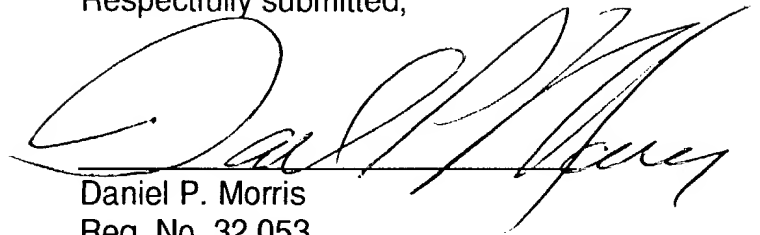
Shinbum article applicants have] prepared drawings or other descriptions of the invention that were sufficiently specific to enable a person skilled in the art to practice the invention.” The Asahi Shinbum article states that applicants’ work was reproduced, by others, thus applicants article was specifically specific for a person of skill in the art to practice applicants’ invention. Also, as stated in a prior response , more than 5,200 articles refer to applicants article showing that applicants enabled the field of high Tc superconductivity In view of applicants remarks the examiner is respectfully requested to withdraw the rejection of applicant’s claims under 35 USC 102(a) and 103 as unpatentable over the Asahi Shinbum article.

In addition to the evidence previously submitted in support of applicants position that their claims are fully enabled, applicants refer to the book “Structural Inorganic Chemistry”, A. F. Wells, Oxford At the Clarendon Press (1962) which provides teaching of the general principles of ceramic science and the structure and properties of perovskite materials.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

If the above-identified Examiner's Action is a final Action, and if the above-identified application will be abandoned without further action by applicants, applicants file a Notice of Appeal to the Board of Appeals and Interferences appealing the final rejection of the claims in the above-identified Examiner's Action. Please charge deposit account 09-0468 any fee necessary to enter such Notice of Appeal.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Daniel P. Morris", written over a horizontal line.

Daniel P. Morris  
Reg. No. 32,053

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598  
(914) 945-3217

CLAIMS (LIKE)

Your search request has found 140,058 PATENTS through Level 1.  
To DISPLAY these PATENTS press either the KWIC, FULL, CITE or SEGMENTS key.  
To MODIFY your search request, press the M key (for MODIFY) and then the ENTER key.

For further explanation, press the H key (for HELP) and then the ENTER key.

Attachment A

CLAIMS (DIAMOND LIKE)

Your search request has found 443 PATENTS through Level 1.  
To DISPLAY these PATENTS press either the KWIC, FULL, CITE or SEGMENTS key.  
To MODIFY your search request, press the M key (for MODIFY) and then the ENTER key.

For further explanation, press the H key (for HELP) and then the ENTER key.

Attachment B

DATE: DECEMBER 26, 1998  
CLIENT: 074  
LIBRARY: LEXPAT  
FILE: UTIL

Your search request is:  
CLAIMS(DIAMOND LIKE CARBON)

Number of PATENTS found with your search request through:  
LEVEL 1... 319

To display the next screen of text of the PATENT you were viewing, press the  
NEXT PAGE key.

To redisplay the screen of text of the PATENT you were viewing, press the  
ENTER key.

For further explanation, press the H key (for HELP) and then the ENTER key.

Attachment C



CLAIMS (HALOGEN LIKE)

Your search request has found 10 PATENTS through Level 1.  
To DISPLAY these PATENTS press either the KWIC, FULL, CITE or SEGMENTS key.  
To MODIFY your search request, press the M key (for MODIFY) and then the ENTER key.

For further explanation, press the H key (for HELP) and then the ENTER key.

Attachment D

CLAIMS (OXYGEN LIKE)

Your search request has found 11 PATENTS through Level 1.  
To DISPLAY these PATENTS press either the KWIC, FULL, CITE or SEGMENTS key.  
To MODIFY your search request, press the M key (for MODIFY) and then the ENTER key.

For further explanation, press the H key (for HELP) and then the ENTER key.

Attachment E

CLAIMS (CERAMIC LIKE)

Your search request has found 79 PATENTS through Level 1.  
To DISPLAY these PATENTS press either the KWIC, FULL, CITE or SEGMENTS key.  
To MODIFY your search request, press the M key (for MODIFY) and then the ENTER key.

For further explanation, press the H key (for HELP) and then the ENTER key.

Attachment

CLAIMS(SILICON LIKE)

Your search request has found 5 PATENTS through Level 1.  
To DISPLAY these PATENTS press either the KWIC, FULL, CITE or SEGMENTS key.  
To MODIFY your search request, press the M key (for MODIFY) and then the ENTER key.

For further explanation, press the H key (for HELP) and then the ENTER key.

Attachment H

CLAIMS (CARBON LIKE)

Your search request has found 31 PATENTS through Level 1.  
To DISPLAY these PATENTS press either the KWIC, FULL, CITE or SEGMENTS key.  
To MODIFY your search request, press the M key (for MODIFY) and then the ENTER key.

For further explanation, press the H key (for HELP) and then the ENTER key.

Attachment G

CLAIMS (NITROGEN-LIKE)

Your search request has found 10 PATENTS through Level 1.  
To DISPLAY these PATENTS press either the KWIC, FULL, CITE or SEGMENTS key.  
To MODIFY your search request, press the M key (for MODIFY) and then the ENTER key.

For further explanation, press the H key (for HELP) and then the ENTER key.

Attachment I

CLAIMS (COPPER LIKE)

Your search request has found 17 PATENTS through Level 1.  
To DISPLAY these PATENTS press either the KWIC, FULL, CITE or SEGMENTS key.  
To MODIFY your search request, press the M key (for MODIFY) and then the ENTER key.

For further explanation, press the H key (for HELP) and then the ENTER key.

Attachment J

# Condensed Matter

## Zeitschrift für Physik B

Volume 64 Number 2 1986



Europhysics Journal

A 20350 D

- P. Marksteiner, P. Blaha, K. Schwarz*  
Electronic Structure and Binding Mechanism of  $\text{Cu}_2\text{O}$  119
- R.D. Williams, S.W. Lovesey, W. Renz*  
Scattering Response of a Phonon Damped Harmonic Oscillator 129
- Ch. Zeller, G. Abstreiter*  
Electric Subbands in Si/SiGe Strained Layer Superlattices 137
- J. Mašek*  
Electronic States in Disordered Systems with Statistical Correlations: Self-Consistent Born Approximation 145
- E. Bauer, E. Gratz, H. Nowotny*  
Transport Properties and Electronic Structure of Nonmagnetic REAg Compounds 151
- K. Winzer*  
Temperature- and Magnetic Field Dependence of the Hall Effect in the Heavy Fermion System  $\text{CeCu}_6$  159
- K.D. Schotte, D. Förster, U. Schotte*  
Can Ultrasonic Sound Attenuation Measurements Elucidate the Coupling of "Heavy Electrons" to the Lattice? 165
- M. Yoshizawa, B. Lüthi, K.D. Schotte*  
Grüneiser: Parameter Coupling in Heavy Fermion Systems 169
- F. Gross, B.S. Chandrasekhar, D. Einzel, K. Andres, P.J. Hirschfeld, H.R. Ott, J. Beuers, Z. Fisk, J.L. Smith*  
Anomalous Temperature Dependence of the Magnetic Field Penetration Depth in Superconducting  $\text{UBe}_{13}$  175
- J.G. Bednorz, K.A. Müller*  
Possible High  $T_c$  Superconductivity in the Ba-La-Cu-O System 189
- R. Bayerer, W. Schneider, J. Heber, D. Mateika*  
Electron-Phonon Relaxation in  $^5\text{D}_4$  of  $\text{Tb}^{3+}$  in Yttrium Aluminium Garnet 195
- R. Bayerer, J. Heber, D. Mateika*  
Crystal-Field Analysis of  $\text{Tb}^{3+}$  Doped Yttrium Aluminium Garnet using Site-Selective Polarized Spectroscopy 201
- S. Lipiński, H. Capellmann*  
On the Magnetization Fluctuations in the Completely Disordered Paramagnetic Medium 211
- G. Moro, P.L. Nordio*  
Rotational Diffusion in Cubic Fields 217
- K.P. Ghatak, M. Mondal*  
Theoretical Analysis of the Gate Capacitance in  $n$ -Channel Inversion Layers on Ternary Chalcopyrite Semiconductors in the Presence of a Quantizing Magnetic Field 223
- P.M. Lam*  
Corrections to Scaling for Branched Polymers 227
- C.M. Arizmendi, L.N. Epele, H. Fanchiotti, C.A. García Canal*  
Ferromagnetic and Antiferromagnetic Properties of the Blume-Capel Model in (1+1) and (2+1) Dimensions 231
- E. Freidkin, P.S. Riseborough, P. Hänggi*  
Quantum Tunneling at Low Temperatures: Results for Weak Damping 237
- G. Hu*  
A Comparison of Master Equation and Fokker-Planck Equation in the Thermodynamic Limit 247
- J. Honerkamp, A. Baumgärtner*  
Anomalous Diffusion on a Fractal: A First Passage Time Problem 253
- Indexed in *Current Contents*
- Evaluated and abstracted for PHYS on STN



Springer International

Attachment K page 1



inse  
1a1te

Attachment K page 2